

CHARACTERIZATION OF REDOX ACTIVE MATERIALS TO ENABLE
ELECTROCHEMICAL SEPARATIONS THROUGH FARADAIC DEIONIZATION

BY

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DISSERTATION

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ABSTRACT

Faradaic deionization (FDI) is an emerging electrochemical separations technique which has received tremendous research interest in the past decade. Established electrochemical separations techniques such as capacitive deionization are limited by low charge storage capacity due to electric double layer charge storage, high energy consumption, and inability to selectively remove specific ions. FDI employs redox active materials with higher charge storage capacity, high selectivity, and offers low energy consumption for the separation process by operating within a moderate potential window. This work is focused on fundamental characterization of materials for FDI to enable a broad range of applications ranging from saltwater desalination, selective ion removal from water streams in agriculture and industry, and carbon dioxide capture from the atmosphere.

Nickel hexacyanoferrate (NiHCF_{Fe}) is chosen as an intercalation host compound for removal of sodium ions from saltwater. To enable high-rate capability, microscopic mechanisms that limit cation intercalation within porous electrodes comprised of NiHCF_{Fe} nanoparticles, conductive carbon additives and polymer binder are investigated. A combination of experimental characterization, particle-scale transport modeling, and porous electrode theory show that slow electron conduction through nanoparticle agglomerates is linked to rate limitations during galvanostatic cycling, while naïve predictions based on crystal-scale diffusion alone suggest rate 4-5 orders of magnitude higher than in experiment. These insights are used to target improvement in electronic conductivity of porous electrodes of NiHCF_{Fe}, resulting in significantly improved desalination performance. Investigation of cation intercalation is carried further from Na⁺

to insertion of Mg^{2+} and Ca^{2+} into NiHCFE in aqueous electrolytes. Capacity fades of up to 75% are observed within 200 cycles during intercalation of $\text{Mg}^{2+}(\text{aq})$ and $\text{Ca}^{2+}(\text{aq})$. A combination of experimental characterization, first-principles electronic structure calculations, statistical mechanics, and lattice-percolation modeling of electron transfer are used to elucidate the mechanisms responsible for the degradation of NiHCFE and its partial retention of capacity. It is quantitatively demonstrated for the first time that Mg^{2+} can displace Ni^{2+} sites within the NiHCFE crystal lattice, leading to structural degradation and removal of ferricyanide and Ni^{2+} ions during electrochemical cycling.

Since NiHCFE is shown to be limited in its application to electrolytes with alkali ions, and has a modest volumetric charge storage capacity, another class of materials – NASICONs (sodium superionic conductors) are investigated. Among NASICONs, sodium vanadium phosphate (NVP) offers three times higher volumetric charge storage density than NiHCFE and potentially minimal degradation in divalent electrolytes. However, during galvanostatic cycling in aqueous electrolyte, complete capacity loss is observed in the first charging cycle due to vanadium dissolution. Titanium alloying is shown to substantially improve stability of NVP, and hence sodium titanium vanadium phosphate (NTVP) is synthesized and characterized. Using electrochemical characterization and first principles calculations, insertion mechanism of Na^+ into NTVP is investigated. Given the high affinity of Na^+ towards NASICON compounds, intercalation of various other alkali, alkaline earth, and ammonium ions is characterized to understand selectivity. NTVP is found to exhibit ion recognition towards Na^+ with a selectivity sequence as $\text{Na}^+ \gg \text{Li}^+ > \text{NH}_4^+ \gg \text{K}^+, \text{Mg}^{2+}, \text{Ca}^{2+}$. This selectivity makes NTVP attractive for excess Na^+ removal for agricultural feed and waste waters in saline regions to prevent micronutrient poisoning

of plants. Operation of NTVP is demonstrated in a custom faradaic deionization cell with mixed K^+ , Na^+ electrolytes.

Extending the application of FDI from cation capture, CO_2 capture from the atmosphere and industrial emissions is explored. Most industrial techniques rely on thermally driven CO_2 separations, which can require up to 10 times the thermodynamic minimum energy requirement. Recent efforts with electrochemical pH swing CO_2 capture aim to lower this energy consumption. By utilizing the pH-dependent solubility of CO_2 in aqueous media, capacitive and pseudocapacitive electrodes have been used to modulate the pH of the feed stream consisting of CO_2 dissolved as bicarbonates in water and desorb pure CO_2 from a low pH stream obtained by reversibly capturing protons. Building upon these concepts, new materials for FDI based CO_2 capture are explored in this work, aimed at significantly improving the rate of CO_2 capture and lowering the overall energy consumption.

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Chapter 1 : Introduction

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1.1 Separations

Separation processes are ubiquitous in nature and industries. The applications are numerous and diverse, ranging from manufacturing high purity chemicals, water purification and desalination, to carbon capture from air to tackle climate change.

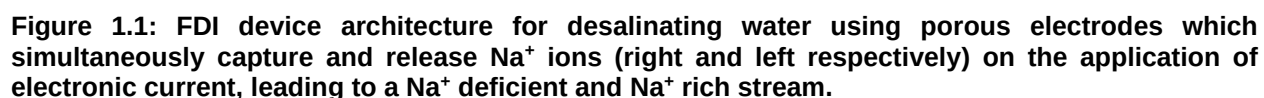
A recent review found that approximately 45 to 55% of the total energy in the USA is used by separation processes, 50% of which are thermal based separations.¹ In most of these processes, energy efficiency is paramount to enable economic feasibility. Further, in applications such as water purification and chemical manufacturing, high degree of selectivity of ion capture is required. Electrochemical separations offer a promising route to achieve these objectives in many applications, and hence have seen increased research interest in the past decade.

1.2 Electrochemical separations

Existing separation processes can broadly be divided into three categories – physical, chemical, and electrochemical. Physical separation processes either involve heating a solution (distillation) or pumping the solution through membranes to overcome the osmotic pressure difference (reverse osmosis) to isolate the dissolved salts from water. However, these methods are not selective to the dissolved species, since no chemical information is used to distinguish the various ions present in the feed solution. Physical

methods can also involve large energy consumption, depending on the concentration and nature of dissolved salts. To overcome these limitations, chemical methods such as precipitation and ion exchange have been extensively researched. While they do achieve selectivity to some degree, both methods operate at very slow rates (from few hours to days) and require the use of additional chemicals (sometimes toxic) to precipitate the species of interest or to regenerate the ion exchange precursors. On the other hand, electrochemical methods can perform separations at much faster rates without introducing additional chemicals into the feed solution. Ions can be captured and removed simply by supplying current and inducing reduction/oxidation reactions. Electrodialysis (ED) and capacitive deionization (CDI) are the two major electrochemical methods developed over the past few decades.² ED uses gas evolution reactions at metallic anode and cathode to induce an electric field, combined with a series of ion exchange membranes to separate anions and cations. In contrast, CDI uses high surface area porous carbon electrodes to capture ions in the electric double layer when an electric potential difference is applied across the anode and cathode. However, both these methods cannot selectively capture ions since species are separated only based on charge. Further ED is an energy intensive process since it uses a large potential difference to split water, whereas CDI is limited to low concentration salt solutions due to the low charge storage capacity of the capacitive process. Therefore, to overcome these limitations in selectivity, energy efficiency and charge storage capacity in existing electrochemical separation techniques, faradaic deionization has come up as a promising alternative in the past few years.

With a battery-like device architecture, faradaic deionization uses redox active materials that can store/release ions under application of an electric current/potential. Enabled by bulk charge storage mechanisms within the electroactive materials, much higher gravimetric and volumetric charge capacities can be achieved compared to CDI processes. Therefore, applications involving separations of concentrated solutions can also be targeted, such as desalination of sea water or brine. Further, high levels of selectivity can be achieved by appropriately choosing and engineering electroactive materials for capturing the species of interest. Fig. 1.1 shows an example of the basic device architecture of a faradaic deionization device for desalinating water, using Nickel hexacyanoferrate (NiHCFe) as the electroactive material for reversible capture of sodium ions.³



In a typical device, porous electrodes comprised of active material, carbon black and polymer binder are casted onto a current collector and saline influent is passed through the device (there are several possible flow configurations, Fig. 1.1 shows a 'flow by' configuration). As shown in Fig. 1.1, the negative electrode comprises of sodium deficient NiHCF_e, which is electrochemically reduced by passing electrons into the material. Consequently, sodium ions from the feed stream are captured by the material, making this half of the feed stream deficient in sodium. Simultaneously, the positive electrode (sodium-rich) is oxidized, releasing sodium into the feed stream. An anion exchange membrane (AEM) allows only chloride ions to pass through – the Cl⁻ ions diffuse from the negative electrode to positive electrode to maintain charge neutrality of the sodium rich stream. Therefore, we end up with a desalinated stream and a concentrated stream. After one charge/discharge cycle, the current direction is reversed, and the desalinated and brine streams are switched. While this example discussed a 'symmetric' cell, i.e., with the same active material on both electrodes, any suitable pair of electroactive materials can be used in principle.

This thesis work focusses on understanding the electroactive materials that can be used in faradaic deionization cells for various applications, ranging from desalination of salt water, selective ion capture in agriculture and industry and carbon capture from the atmosphere.

Chapter 2 : Identifying rate limiting mechanisms in porous electrodes of Prussian blue analogues in aqueous electrolytes

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2.1 Prussian Blue Analogues for faradaic deionization

Prussian Blue (PB) and its analogues (PBAs) have attracted a great deal of research interest over the past decade. These are mixed-valence, intercalation host compounds (IHCs) with a nominal chemical formula $A_xMFe(CN)_6$, where A is a monovalent cation being intercalated, M is a divalent transition metal, and the degree of intercalation x varies between 0 to 1 corresponding to Fe^{3+} and Fe^{2+} states, respectively. Fig. 1.2 shows an example of the crystal structure of a PBA.

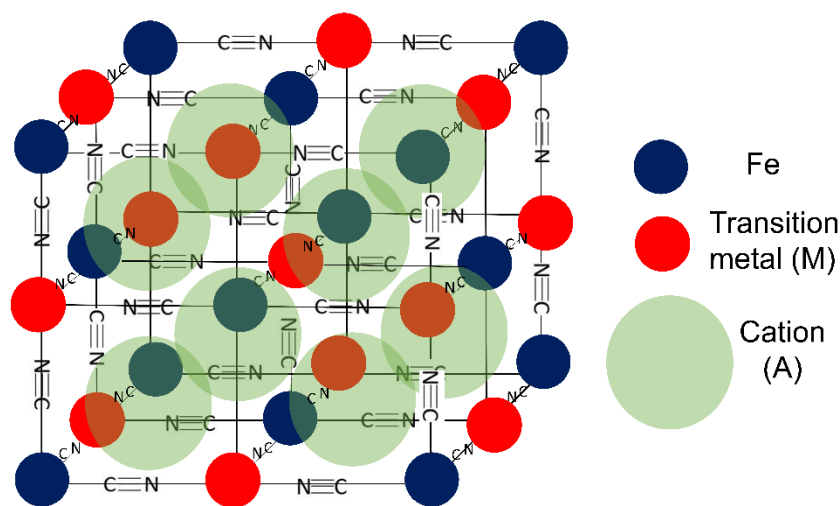


Figure 2.1: Face centered cubic crystal structure of a fully intercalated PBA

PBAs have shown high charge storage capacity, fast, reversible intercalation kinetics and long cycle life when operated in aqueous and non-aqueous electrolytes with a remarkable variety of cations, ranging from alkali and alkaline earth metal ions,^{4–6} organic ions such as NH_4^+ ,⁷ transition metals such as Cu^{2+} , Co^{2+} , and Ni^{2+} and even heavy metallic ions

such as Pb^{2+} , Y^{3+} , and Sm^{3+} .⁸ This versatility makes them highly attractive for grid scale energy storage,^{5,6,9–11} radioactive waste removal,^{12–15} and various other applications demanding reversible ion storage.^{16–21} Therefore, these materials are highly attractive from the perspective of faradaic deionization as well.

2.1.1 Selecting appropriate PBA for aqueous faradaic deionization

Nickel hexacyanoferrate (NiHCF_e) is a particularly suitable active material for faradaic deionization of saltwater when compared to other PBAs because it shows excellent electrochemical performance in monovalent aqueous electrolytes. Fig. 1.2 shows the potential window of operation and the potential at 50 % state-of-charge (SOC) for various PBAs during galvanostatic cycling with $\text{Na}^+_{(\text{aq})}$.²²

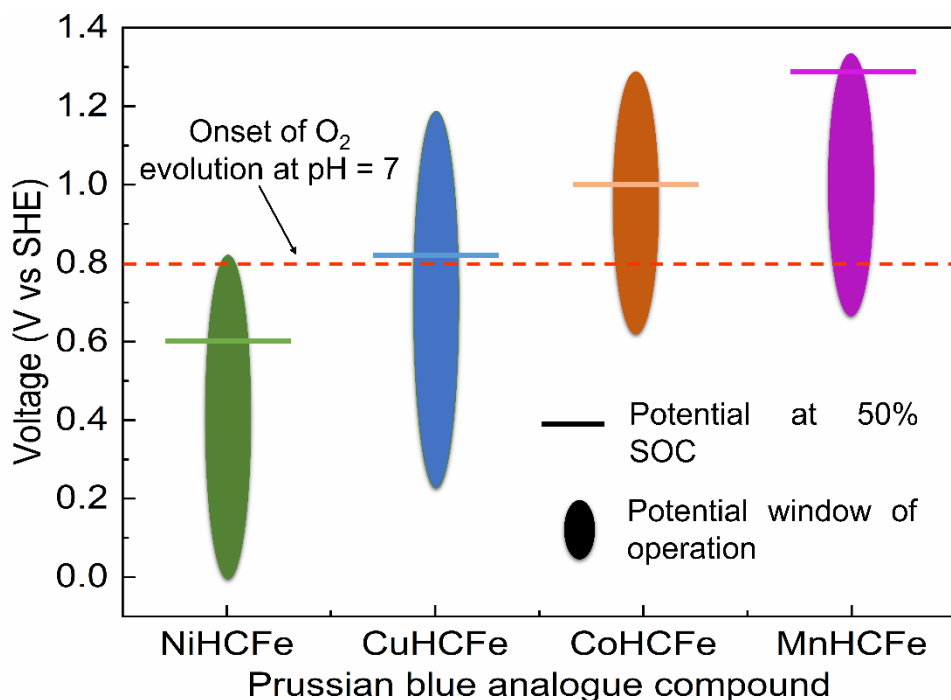


Figure 2.2: Operating potential window for various Prussian blue analogues in aqueous electrolytes at pH 7

While NiHCF_e intercalates Na^+ well below the O_2 evolution potential at neutral pH, other PBAs intercalate it at much higher potentials, close to or beyond 0.8 V vs SHE. Moreover,

NiHCFE exhibits a charge storage capacity of 60 - 70 mAh/g while retaining 100 % capacity and coulombic efficiency over thousands of cycles.^{4,23} CuHCFE shows similar capacity and rate capability, but at potentials nearly 200 mV higher than NiHCFE.¹⁰ This property of CuHCFE could ultimately result in higher overall energy consumption and capacity loss during desalination due to O₂ evolution. Although CoHCFE and MnHCFE exhibit almost double the charge capacity compared to NiHCFE, they show poor rate capability and low coulombic efficiency in aqueous electrolytes.²⁴ Further, a significant portion of the charge capacity for (Co/Mn)HCFE can only be accessed beyond the electrolytic stability window of water, which makes these materials undesirable for application in faradaic deionization, again due to the competition with O₂ evolution reaction. Therefore, NiHCFE is the most suitable PBA to investigate for faradaic deionization in aqueous electrolytes.

2.2 Understanding transport in porous electrodes

In electrochemical desalination and related applications, thick, porous electrodes with high mass loading of the active material are needed to maximize areal charge storage and to deliver high charge capacity at large current densities. For example, electrochemical water desalination using the newly emerging cation intercalation desalination cells^{3,25–29} demands high rate capability from the intercalation host compounds (IHCs) being employed. Figure 2.1 (a) shows the variation of material cost of desalination (in \$ per m³/day) of 500 mM NaCl as a function of specific currents applied, assuming a nominal charge capacity of ~60 mAh/g is delivered at all currents. As the unit cost of manufacturing the IHC increases (calculated using raw material costs of the metals in each IHC³⁰), the required specific current increases to keep the material cost

same. To minimize the capital cost of active materials involved, electrodes must desalinate water at large specific currents, which requires high rate capability. In the context of energy storage, high rate capability is needed to enable flexible storage in peak-shaving on the electric grid³¹ and for pulsed-power operation of electric vehicles.³² Transport and kinetic processes must be thoroughly understood to identify rate-limiting mechanisms to improve *in-operando* rate capability. However, current research lacks systematic understanding of electron and cation transport in porous electrodes containing PBA nanoparticles (NPs). Although there have been several studies^{33–39} to characterize cation intercalation reactions, electronic conduction, and ambipolar diffusion in PBAs, most focus on thin films of thickness ranging from 0.5 to 1.0 μm . Nevertheless, these studies have provided valuable insights into transport processes within PBAs. For instance, cation intercalation reaction kinetics were reported to follow a three-stage mechanism involving adsorption and desorption of anions.^{33,34} Also, localized hopping has been confirmed as the mechanism of electron conduction in PB and in its other redox forms,³⁶ while the current/voltage response of dry thin films reveals a poor electronic conductivity of $5 \times 10^{-5} \text{ S/m}$.³⁵ The diffusion coefficients of Na^+ and Rb^+ in nickel hexacyanoferrate (NiHCF)³⁸ and K^+ in copper hexacyanoferrate³⁷ and PB thin films³⁹ have all been reported as $\sim 10^{-9} \text{ cm}^2/\text{s}$ using cyclic voltammetry, chronoamperometry, impedance spectroscopy and coulometry. However, the coupling between cation diffusion and electron hopping inhibits isolation of these two effects using electrochemical characterization techniques.³⁷ Apart from the magnitude of the diffusion coefficient, its variation with the degree of intercalation x (DOI) can provide information about the mechanisms involved. For instance, PB thin films exhibit a non-monotonic variation of

the K^+ diffusion coefficient versus DOI with a minimum value near 50% DOI,³⁹ an effect that was previously explained *ad hoc* using non-equilibrium thermodynamics with a binary solution model for chemical potential.³⁹ In this work, we study transport in slurry-cast porous electrodes comprised of NiHCF NPs containing conducting additive (carbon black) and polymer binder (PVDF). We characterize the variation of diffusion coefficients with the DOI and analyze the obtained profile to understand the rate limiting mechanisms. Amongst the various electroanalytical techniques used to measure cation diffusion coefficients, electrochemical titration techniques offer the distinct advantage of providing diffusion coefficient as a function of DOI in addition to measuring the quasi-equilibrium potential profiles. The potentiostatic intermittent titration technique (PITT) has been employed extensively to characterize diffusion in a wide range of electroactive materials. Although this technique was originally developed to analyze thin films of Li-Al alloys,⁴⁰ it has also been used to characterize Li^+ intercalation in thin film electrodes of graphite^{41,42} and in transition metal oxides,^{43–49} and of Na^+ and K^+ intercalation in NMO⁵⁰ and PB,^{39,51} respectively. However, to apply this technique to porous electrodes, a modified theory of current response is required that accounts for nanoparticulate morphology.¹ Recently, Li

¹Early PITT theories assume infinitely fast reaction kinetics and model using dense thin film thickness as a parameter.⁴⁰ This assumption introduces significant errors if directly applied to porous electrodes. Approximating porous electrodes as dense thin films can lead to spurious measurements of diffusivity due to (1) finite porosity levels that can range between 30 to 50%, (2) the length-scale for cation transport from electrolyte into a NP can be much smaller than the overall thickness of the electrode,¹⁵⁹ and (3) NPs have orders of magnitude larger surface area for intercalation kinetics than a thin film of the same mass.

et al.⁵² introduced and applied a modified theory for PITT that models porous electrodes using a homogenous distribution of spherical active particles with finite interfacial kinetics. They predicted the temporal current response for graphite (MCMB) electrodes subject to an incremental potential step with which the Li^+ diffusion coefficient and the intercalation exchange current density were obtained as fitting parameters using their PITT theory. The interplay between electronic conduction, agglomeration, and cation diffusion within redox-active particles has been explored previously in the context of rechargeable batteries. For instance, certain Li-ion and Na-ion battery materials (such as LiFePO_4 and $\text{NaTi}_2(\text{PO}_4)_3$) are ohmic conductors with either low electronic conductivity or are semiconductors.^{10,53,54}

To overcome such limitations, nanoparticulate material formats,⁵⁵ doping,⁵⁶ and carbon coating of NPs^{57–59} have been used. Further, the agglomeration of NPs has been shown to influence the local rate of Li^+ intercalation.^{60–63}

In this work, we show that electron conduction is responsible for the apparent diffusion in porous electrodes containing NiHCFe NPs. We show that modulation of NiHCFe NP agglomerate size affects galvanostatic rate capability in electrodes prepared with two different electrode fabrication procedures. Rate capability is found to be more sluggish than expected if Na^+ diffusion through individual NPs was limiting. Accordingly, we characterized Na^+ diffusion in aqueous electrolyte using PITT to determine the apparent diffusion time scale ($t = R^2 / D_{app}$ with radius R and apparent diffusion coefficient D_{app}) as a function of the DOI x for both types of electrodes. We measure two-fold faster diffusion time scales for the unmilled relative to milled electrodes, revealing that the path length for diffusion is not dependent on nanoparticle size, but rather on size of the nanoparticle

agglomerates. Inspired by these findings, we develop a micro-scale theory that links the variation of apparent diffusion time scale with the degree of intercalation to measurable properties, namely the electronic conductivity and differential capacitance of NiHCFe nanoparticle agglomerates. We compare diffusion coefficients predicted from this theory to the corresponding experimental values from PITT. Lastly, we compare experimental rate capability and polarization measurements during galvanostatic cycling with simulations of diffusion through a single spherical electroactive medium incorporating $D_{app}(x)$ predicted by theory.

2.3 Experimental methods

2.3.1 Synthesis and characterization of sodium deficient NiHCFe nanoparticles

100 mL of 0.2M NiCl₂ (Alfa-Aesar) and 100 mL of 0.1M K₃Fe(CN)₆ (Sigma-Aldrich) were simultaneously added dropwise into 200 ml of 1.2M NaCl (Sigma-Aldrich) and stirred vigorously at room temperature throughout the duration of the reaction. The obtained NP dispersion was sonicated for half an hour and aged overnight. These NPs were centrifuged and rinsed with deionized (DI) water and ethanol several times followed by heating in an oven at ~80°C for approximately 12-16 hours to evaporate any solvent. The dried NPs were characterized using CHN and ICP-AES analysis (PerkinElmer 2400 Series II and Perkin Elmer 2000DV), powder X-ray diffraction (Siemens/Bruker D-5000) and scanning electron microscopy (JEOL 6060LV, Hitachi S 4700).

2.3.2 Fabrication of electrodes

The dry mixing of active particles with carbon black (C45, Timcal, Switzerland) was performed using two different methods: (1) using an agate mortar/pestle to grind and mix until a macroscopically homogenous powder was observed (referred to as “unmilled”) and

(2) grinding active material and carbon black powders together in a vortex mill with 5mm steel balls (Ultra Turra-X, IKA) at 6000 rpm for 10 to 15 minutes (referred to as “milled”). Polyvinylidene fluoride binder (PVDF, Sigma Aldrich) was mixed with N-methyl-2-pyrrolidone (NMP, Sigma Aldrich) to form a 16.2 wt.% solution. Active material and carbon black powders were further added to this solution and mixed in a planetary mixer (Thinky, ARE-310) for 30 minutes. The resulting slurry was cast onto graphite foil current collectors using a doctor blade and film applicator (Elcometer 4340). These electrodes were immersed in deionized water overnight for wet phase inversion⁶⁴ and were subsequently dried in a fumehood, followed by heating in an oven at 70°C for 2-3 hours. In all cases the composition of the electrodes was 79% active material, 10.5% carbon black, and 10.5% PVDF, with a dried thickness of approximately 60-70 μm . NiHCF mass was 5-6 mg/cm^2 for both types of electrodes. Images were obtained using a scanning electron microscope (JEOL 6060LV).

2.3.3 Electrochemical characterization

Both galvanostatic cycling and PITT experiments were performed in a three-electrode flooded cell setup using a Biologic VMP3 potentiostat using 1 cm^2 circular working electrodes, Ag/AgCl reference electrodes (0.199V vs. SHE, Pine Research), and a graphite rod (Gamry) as a counter electrode. Before starting PITT experiments, the electrodes were cycled at low current density (0.05 mA cm^{-2}) at least once in 1M NaCl to exchange residual intercalated cations in the host structure (K^+ and Ni^{2+}) with Na^+ . In PITT experiments, the electrode potential was stepped during charging between -0.1 and 0.6 V vs. Ag/AgCl in 5 mV increments until the current value reached approximately 50 nA/mg

at each step. The electrodes were then held at open circuit for one hour and discharged from 0.6 V using the same protocol until -0.1 V was reached.

2.3.4 Electronic conductivity measurement

NiHCFe powders were compactly filled in a CR2032 coin cell casing. The inner surfaces of both caps were painted with carbon to minimize contact resistance with the particles. After tightly enclosing the powders, they were crimped at high pressure of 1.43T from both sides to yield a final internal thickness of 2.1 mm for the compact. The powders occupied a volume fraction of 49.7% on average. The resistance and effective electronic conductivity were calculated using the slope of the measured current/voltage curve.

2.4 Insights from potentiostatic titration and particle scale modeling

We first discuss results from experimental characterization of NiHCF porous electrodes by analyzing material structure, galvanostatic cycling, and apparent diffusion using PITT. In the subsequent section we present an electron-limited version of porous electrode theory to explain the trends observed from PITT and finally present galvanostatic-cycling simulations using this theory applied to a single electroactive sphere for validation.

2.4.1 Physical and electrochemical characterization

The structure and composition of active material powder was characterized using X-Ray diffraction and elemental analysis. The stoichiometry of as synthesized NPs, normalized to one Ni unit, was inferred to be $\text{Na}_{0.42}\text{Ni}(\text{Fe}_{0.92}(\text{CN}_{0.95})_6)_{0.73} \cdot 4.04\text{H}_2\text{O}$ based on the weight fractions of Na, Ni, Fe, C, N, and N. This formula deviates from the nominal stoichiometry of $\text{NaNiFe}(\text{CN})_6$, suggesting that (1) $[\text{Fe}(\text{CN})_6]^{3-}$ vacancies originate during synthesis due to the extremely rapid precipitation reaction and (2) a deficiency of Na^+ ions results from partial intercalation of Ni^{2+} in Na^+ sites. Analysis of powder XRD data (Fig. 2.1(b)) reveals

that the crystal structure belongs to the Fm-3m space group with a unit cell lattice parameter of 10.2 Å in good agreement with previous literature (Fig 2.1(c)).⁴ Figure 2.1(d) shows an SEM image of dried NPs, where primary particle sizes range between 20 to 50 nm with an average size of approximately 30 nm similar to previous reports.^{4,9}

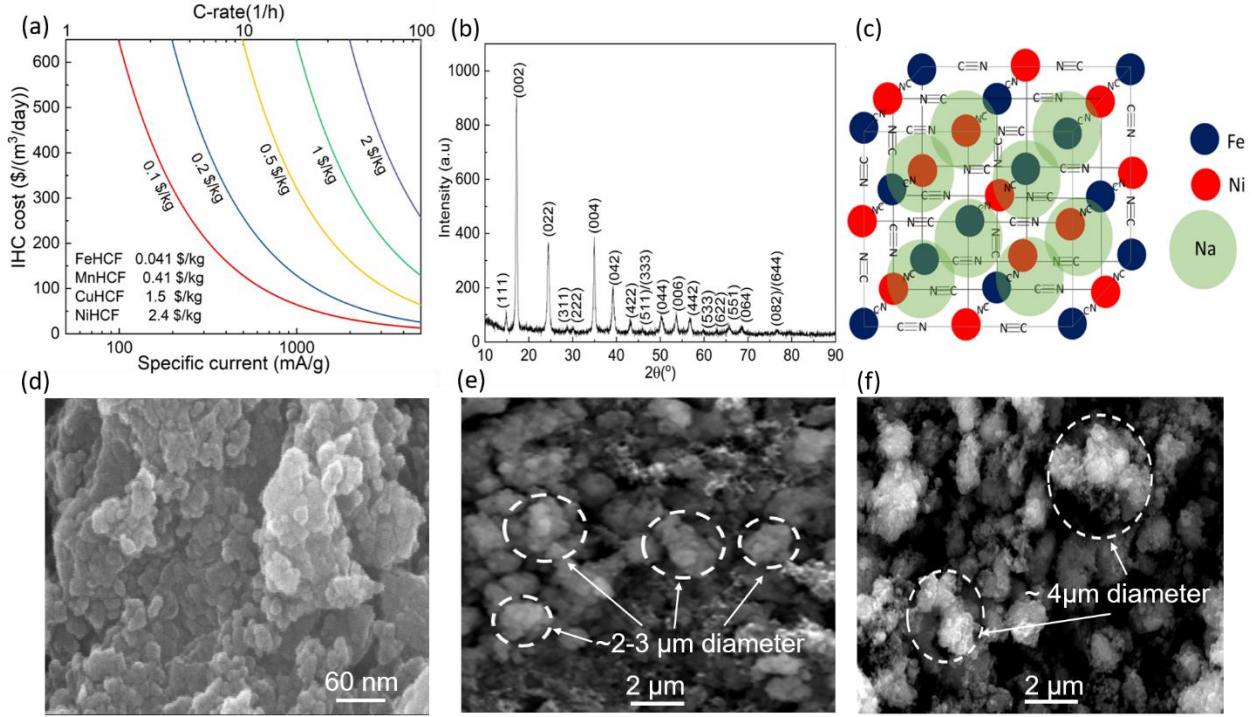


Figure 2.3: (a) Variation of the capital cost of intercalation host materials with specific currents for electrochemical desalination of sea water (500 mM NaCl) using PBAs. (b) X-Ray diffraction pattern of as synthesized sodium-deficient NiHCF, and (c) a schematic of crystal structure of fully intercalated NiHCF. (d) FE-SEM image of NP agglomerates and FE-SEM images of NiHCF NP agglomerates in carbon black matrix for (e) unmilled and (f) milled electrodes.

Considering both the small length scale through which Na^+ ions must diffuse into NiHCF NPs (20-50nm) and the large interstitial sites for intercalation of Na^+ ions (0.5 nm based on unit cell dimensions) compared to the solvated ionic radius of Na^+ (0.3 nm⁶⁵), the rate of crystal scale diffusion of Na^+ is expected to be ultra-fast. Based on previously measured diffusion coefficients for NiHCF thin films³⁸ and a simple analytical model⁶⁶ we expect to achieve 50% charge capacity utilization at a C-rate of 750 s⁻¹ for 30 nm diameter NPs. In contrast with this expectation we find presently that, when using the

same batch of NiHCF NPs having the same NP size distributions, two-fold higher rate capability and three-fold faster diffusion time scales at 50% DOI are achievable when NP agglomerate radius is reduced by two-fold (Figs 2.1(e,f) and 2.2) . Further, we observe dramatically lower rate capability of 30-50 h⁻¹ for 50% charge capacity utilization, which is 4-5 orders of magnitude slower than expected if crystal-scale diffusion were rate limiting. Subsequently, we explore the role of NP agglomeration in determining rate capability.

To experimentally investigate the effect of NP agglomeration on the rate capability of NiHCF electrodes, we adopted two different procedures to mix active-material powders with carbon black, both of which were performed dry (i.e., prior to suspension in NMP). We refer to the resulting electrodes as “unmilled” and “milled” (see Experimental Methods) throughout the remainder of this article. SEM images in Figures 2.1(e) and 2.1(f) show that average agglomerate sizes are smaller in the unmilled electrode (2-3 μm) than the milled one (4-5 μm). This finding is counterintuitive because we expected the vortex milling process to yield smaller agglomerate radii. Note that SEM imagery here is highly qualitative since it is difficult to distinctly image agglomerates and obtain their precise size distribution in such a complex heterogenous matrix. Nonetheless the images provide an approximate comparison of agglomerate sizes.

All experiments were performed using concentrated NaCl electrolyte (500 mM) with salinity typical of seawater and on the order of that used in aqueous rechargeable sodium ion batteries, similar electrode thicknesses, loading and porosity. The same batch of NPs was used for unmilled and milled electrodes, and, thus, any differences in their galvanostatic cycling performance must arise due to differences in microstructure

resulting from the electrode fabrication procedure used. Figures 2.2(a) and 2.2(b) show the results of galvanostatic cycling of both electrodes in 0.5M NaCl electrolyte. The unmilled electrode shows a maximum charge capacity of 68 mAh/g and 50% charge capacity utilization at 50C, whereas the milled electrode shows significantly lower charge capacities and only 14% charge capacity utilization at 50C. Examination of potential versus time curves (Figs. 2.2(c) and (d)) reveals that milled electrodes produce greater polarization than unmilled ones at the same current density or C-rate. Despite these differences both electrode types show excellent coulombic efficiency at all current densities and exhibit negligible capacity fade over approximately 100 charge/discharge cycles.

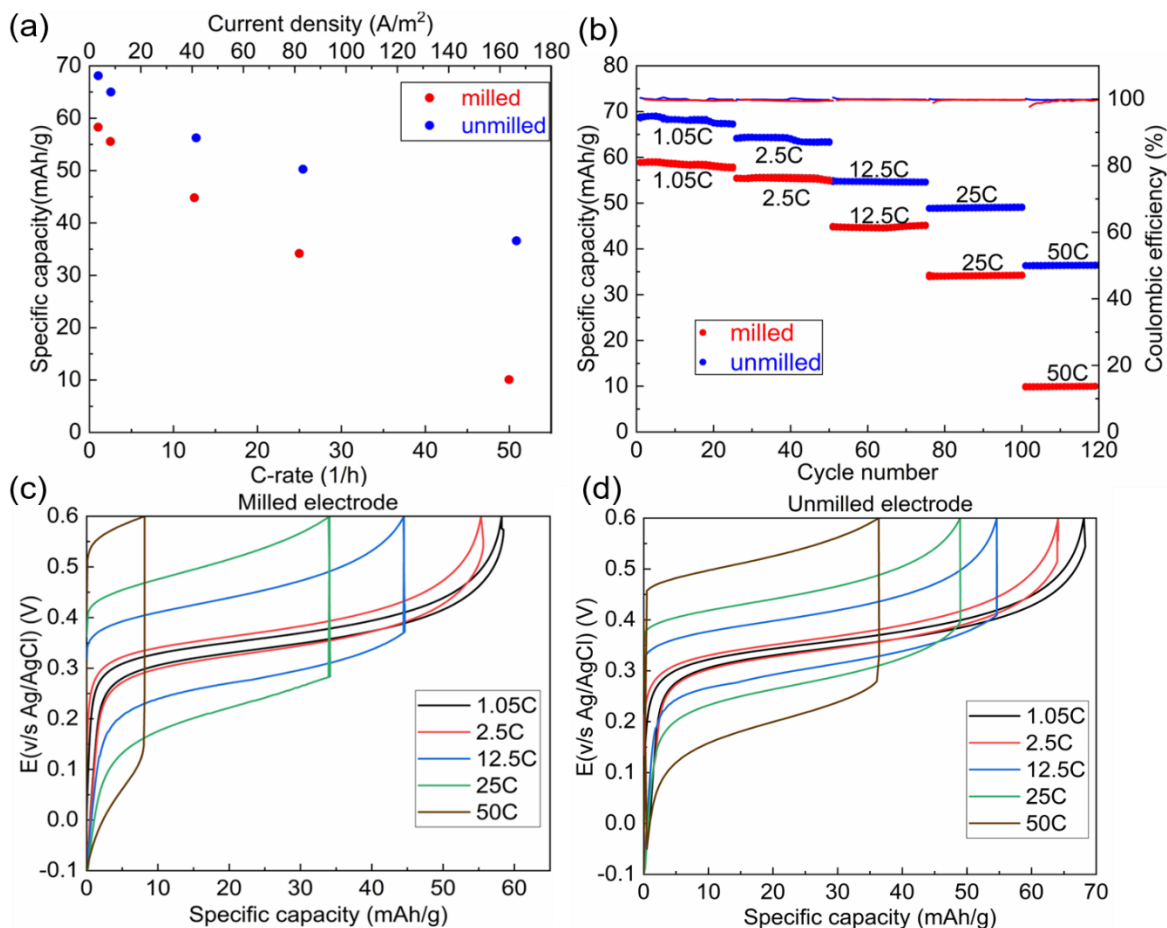


Figure 2.4: (a) Variation of specific capacity of unmilled and milled electrodes with cycle number at different C-rates and (b) specific capacity as a function of C-rate and current density for milled and unmilled electrodes. Voltage versus specific capacity for (c) unmilled and (d) milled electrodes.

We now explore the roles of cation diffusion and NP agglomeration in determining the galvanostatic performance of both milled and unmilled electrodes (1) by measuring the composition-dependent Na^+ diffusion coefficient using PITT and (2) by predicting galvanostatic cycling curves using this measured data in a continuum diffusion model. To determine diffusion coefficient values from PITT we idealize the NiHCF_e material in which Na^+ ions diffuse as a spherical electroactive phase embedded within an electronically conductive matrix. This simplification is routinely employed in porous electrode modeling of Li-ion battery electrodes.^{66–68} When such material is subjected to PITT or galvanostatic

cycling, a natural “diffusion time scale” of $\tau = R^2/D_{app}$ arises while solving for concentration profiles in the active material, where R is the radius of the particles and D_{app} is the apparent diffusion coefficient measured from PITT. Furthermore, resistive processes can manifest in PITT data, including through the effects of interfacial reactions,⁶⁹ contact resistance between NP agglomerates and the percolating conductive-carbon backbone, and electron conduction through the backbone itself. To incorporate these effects we adopt the PITT model developed previously⁵² to fit current as a function of time at each potential step to obtain diffusion coefficients. Here, the short time current I varies with time t in proportion to the total charge transferred Q for the entire potential step as:

$$I(t) = \frac{3Q}{t} \left(-\frac{Bi}{Bi-1} \left[1 - \operatorname{erfc} \left(\sqrt{\frac{t}{\tau}} \right) \right] + \frac{Bi^2}{Bi-1} \exp \left(\frac{t}{\tau} (Bi-1)^2 \right) \operatorname{erfc} \left((Bi-1) \sqrt{\frac{t}{\tau}} \right) + \frac{Bi^2 - 2Bi}{Bi-1} \exp \left(2(Bi-1) + \frac{t}{\tau} (Bi-1)^2 \right) \operatorname{erfc} \left(\sqrt{\frac{t}{\tau}} + (Bi-1) \sqrt{\frac{t}{\tau}} \right) \right) \quad (2.1)$$

which also depends on the electrochemical Biot number Bi and the diffusion time-scale $\tau = R^2/D_{app}$. While in Ref. 49 this PITT model incorporated finite interfacial kinetics using a Biot number defined in terms of kinetic exchange current density, we introduce a generic definition of the Biot number that accounts for an area-specific charge-transfer resistance R''_{ct} (in units of $\Omega\text{-m}^2$) at the surface of an electroactive sphere, where $Bi \equiv -R(\partial\phi_{eq}/\partial x)/(R''_{ct}D_{app}q_{max})$. In the present context Bi is a ratio of the characteristic interfacial potential drop due to charge transfer into the electroactive sphere relative to the corresponding variation in equilibrium potential ϕ_{eq} induced by gradients in the degree-of-intercalation x within the electroactive sphere having a maximum volumetric charge capacity q_{max} (analogous to the thermal Biot number for heat convection over a

thermally conductive sphere). Thus, a Biot number greater than unity implies that interfacial potential drop is smaller than the potential drop inside of the redox-active material.^{52,70}

Using this theory PITT experiments were performed to characterize diffusion in each electrode. Figure 2.3(a) shows an example sequence of potential steps with the corresponding current response in the inset. The variation of equilibrium potential ϕ_{eq} with DOI x was determined by normalizing the accumulated charge for each potential step by the maximum charge capacity Q_{max} , while ϕ_{eq} was determined by the magnitude of the particular potential at which the step occurred (Fig. 2.3(b)). Comparison of the present empirical curve to a regular solution model²⁶ (used in previous modelling of NiHCF_e) shows a maximum deviation of 35 mV for $x \rightarrow 0$, while for $x > 0.4$ agreement within 20mV is observed. We specifically observe that there is a critical concentration below which the regular solution model significantly deviates from the experimental equilibrium potential curve, both in this work and previously reported low rate cycling data.⁴ Therefore, we fitted an excess equilibrium potential function to the measured potential to account for deviations from regular solution behaviour (Figure 2.3(b)). This function reduces the maximum deviation between experimental and analytical values from 35 mV to 2mV for x tending to 0.

At each potential step the current response data measured during PITT were fitted to obtain τ and Bi values as a function of x for unmilled and milled electrodes. In all cases the regression coefficient of determination was between 0.95 and 1.00, indicating very good agreement between experimental and fitted data. The Biot numbers at each step ranged from 5 to 50, implying that diffusion is the limiting mechanism. However, we

observed that the charge transfer resistance was practically constant with the DOI for both types of electrodes, instead of a parabolic profile expected for charge transfer limited by intercalation kinetics.⁷¹ This finding suggests that our PITT experiments were probing processes other than intercalation kinetics that we attribute to electron transfer from the conducting backbone into NPs, among other effects. R''_{ct} was 800 $\Omega\text{-cm}^2$ for the unmilled electrode and 200 $\Omega\text{-cm}^2$ for the milled one, both of which are an order of magnitude higher than that found for Li^+ intercalation in graphite (32 $\Omega\text{-cm}^2$).⁵² This finding, together with the complex kinetic sequence recently proposed for PBA intercalation,³⁴ suggests that further characterization is needed to accurately quantify exchange current density. Although it is difficult to determine the precise origin of charge transfer resistance, the present Biot numbers nevertheless indicate that diffusion (not charge transfer) limits rate capability.

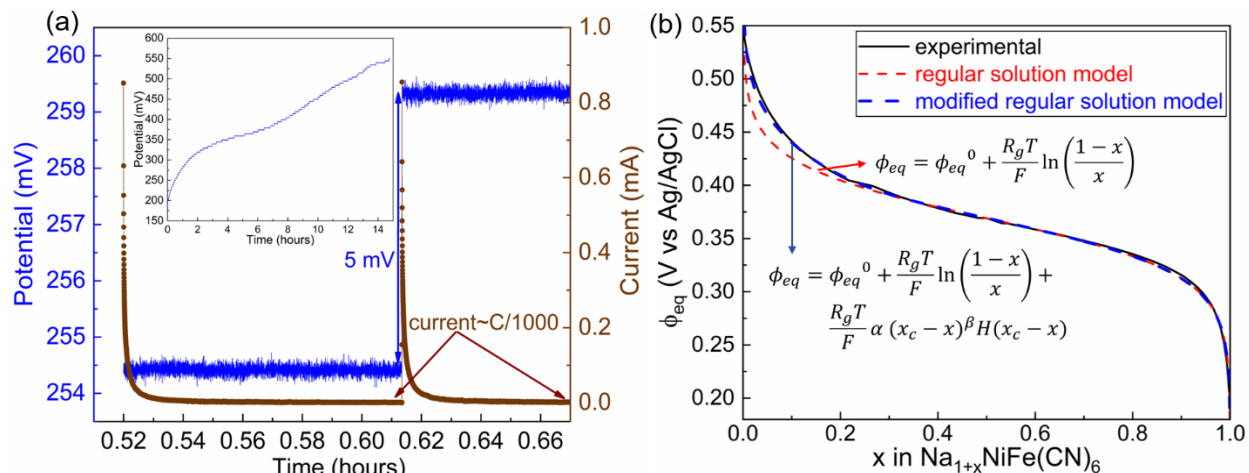


Figure 2.5: (a) Example of a PITT procedure performed during charging. The inset shows a complete charging profile during PITT and (b) experimental equilibrium potential profile obtained from PITT experiment compared with the regular solution model and a modified version thereof, as a function of the degree of intercalation. In the modified model $\alpha=12.6$, $\beta=2.32$, $x_c=0.358$, and $H(\dots)$ is the Heaviside function.

Figure 2.6 shows the inverse diffusion time scales obtained from PITT ($1/\tau = D_{app}/R^2$) as a function of DOI x for both electrodes. To minimize the accumulation of experimental error in the reported values we performed a series of PITT sequences in both intercalation and de-intercalation modes several times. The values presented here from $x = 0.0$ to 0.5 were obtained from intercalation experiments, while for $x = 0.5$ to 1.0 data were obtained by de-intercalation. Appendix B includes data analysis from our PITT experiments in greater detail. The resulting profile of $1/\tau$ is non-monotonic and shows maximum values at the terminal degrees of intercalation ($x \rightarrow 0.0$ and $x \rightarrow 1.0$) and a minimum value at $x \approx 0.5$. This trend is qualitatively similar to the diffusion-coefficient profiles obtained with PB thin films.^{39,51} Among the two electrode types tested, unmilled electrodes show approximately two-fold higher $1/\tau$ at $x \approx 0.5$ despite using NiHCF with the same NP size distribution and composition. This finding is inconsistent with the proposition that the apparent diffusion rates are limited by the crystal scale diffusion of cations because the same $1/\tau$ values would be expected irrespective of the electrode fabrication procedure if

the same NPs are used. Thus, other factors than NP size are responsible for the observed enhancement in apparent diffusion in unmilled electrodes. We later show, by way of comparison with an electronically limited version of porous electrode theory, that an apparent diffusion process through nanoparticle agglomerates is responsible for this observation, rather than nanoscale diffusion through NiHCF_e nanoparticles themselves. Later, we use porous electrode theory (Eqns. 2.2, 2.3 and 2.4) in combination with microscopy (Figs. 2.1(d) and (e)) and independent measurements of the effective electronic conductivity of NiHCF_e NP agglomerates to show that slow electronic conduction induces a dependence of apparent diffusion rates on the size of NP agglomerates.

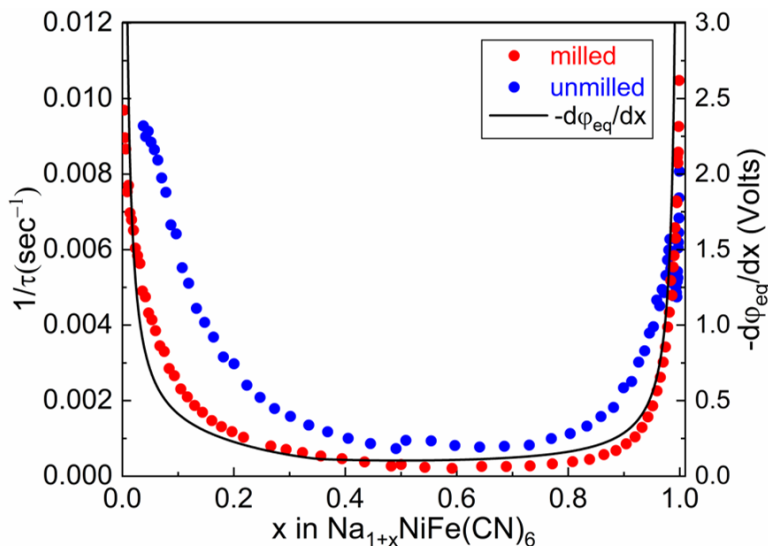


Figure 2.6: Inverse diffusion time scales ($1/\tau = D_{app}/R^2$) for unmilled and milled electrodes. The derivative of equilibrium potential Φ_{eq} with the degree of intercalation x is shown as well.

2.4.2 Theory and modeling to explain trends in diffusion time scales with respect to intercalant fraction

We now use theory to explain the origin of apparent diffusion processes by assuming that electronic conduction through agglomerates of NiHCF_e NPs is the transport-limiting mechanism. In reality, crystal-scale gradients in the DOI persist within any given NiHCF_e

NP, but here we assume that DOI variations within any given NP are small in comparison with the difference in DOI between different NPs at distinct locations within the same agglomerate. This scenario is illustrated in Figure 2.5(a), where the local value of x varies substantially between NPs and x is practically constant within a given NP. To model this heterogeneous system of NPs using continuum theory we consider a homogenized version of agglomerates wherein NiHCFE NPs occupy a volume fraction v_s on average in the agglomerate and possess a local average DOI $\langle x \rangle$ at any radial position r inside the agglomerate. In the past we have used such homogenization procedures to model the dynamics of cation intercalation desalination^{26,72} and semi-solid flow^{73,74} electrodes. Here, the homogenized electronic current density $\langle \vec{i}_s \rangle$ through the agglomerate is $-\sigma_{s,eff} \nabla \phi_s$, where $\sigma_{s,eff}$ is the effective electronic conductivity and ϕ_s is the local homogenized electronic potential. Electronic conduction is constrained by the local reaction current density i_n at the surface of NiHCFE NPs by electronic current conservation applied to a representative volume element, which produces the following equation:

$$\nabla \cdot (-\sigma_{s,eff} \nabla \phi_s) + a v_s i_n = 0 \quad (2.2)$$

where a is the volumetric surface area of NiHCFE NPs. We can apply mass conservation to determine the evolution of the average DOI $\langle x \rangle$ at a certain location within the agglomerate:

$$\frac{v_s q_{max}}{F} \frac{\partial \langle x \rangle}{\partial t} = \frac{a v_s i_n}{F} \quad (2.3)$$

Here, q_{max} is the maximum charge capacity per unit volume of NiHCFE and F is Faraday's constant. Assuming sufficiently fast interfacial kinetics (as evidenced by experimental Biot numbers exceeding unity) the overpotential at the NiHCFE/electrolyte interface is

negligible, in which case the local homogenized electronic potential ϕ_s is related to the reduced electrochemical potential of Na^+ ions in the electrolyte and the equilibrium potential for intercalation of Na^+ ions ϕ_{eq} as $\phi_s = \phi_e + \phi_{eq}$. For the limit in which the effective ionic conductivity of the electrolyte κ_{eff} is much greater than the effective electronic conductivity $\sigma_{s,eff}$ local homogenized electronic potential gradients are equal to equilibrium potential gradients. Invoking these assumptions and combining Eqns. 2.2 and 2.3 to eliminate i_n , we find the following Fickian evolution equation for the local average DOI $\langle x \rangle$ after applying the chain rule to express the equilibrium potential gradient $\nabla\phi_{eq}$ in terms of the local average DOI gradient $\nabla\langle x \rangle$:

$$\frac{\partial\langle x \rangle}{\partial t} = \nabla \cdot (D_{app}(x)\nabla\langle x \rangle) \quad (2.4)$$

Here, the apparent diffusion coefficient D_{app} varies in proportion to the effective electronic conductivity of agglomerated NPs $\sigma_{s,eff}$ and in proportion to $\partial\phi_{eq}/\partial x$:

$$D_{app} = \sigma_{s,eff}(-\partial\phi_{eq}/\partial x)/q_{max}. \quad (2.5)$$

Here, D_{app} varies as a function of the DOI x as a result of the variations of $\partial\phi_{eq}/\partial x$, consistent with our earlier experimental observation of similar scaling with x between these two parameters (see Fig. 2.6). We also note that this result can be interpreted as a resistive/capacitive apparent diffusion phenomenon since $1/D_{app} = \rho_{s,eff}C_{diff}$, where $\rho_{s,eff}$ is the effective electronic resistivity of NP agglomerates and C_{diff} is the volumetric differential capacitance for Na^+ intercalation in NiHCFe equal to $(-\partial\phi_{eq}/\partial x)/q_{max}$. Note that electronic conductivity is the only *transport property* in this expression. A similar “electrical diffusivity” term was first introduced by Johnson and Newman⁷⁵ during modelling of porous carbon electrodes for desalting water, and similar analysis was later

used by Smith and co-workers⁷⁴ to describe transient Li^+ intercalation in semi-solid suspensions of $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

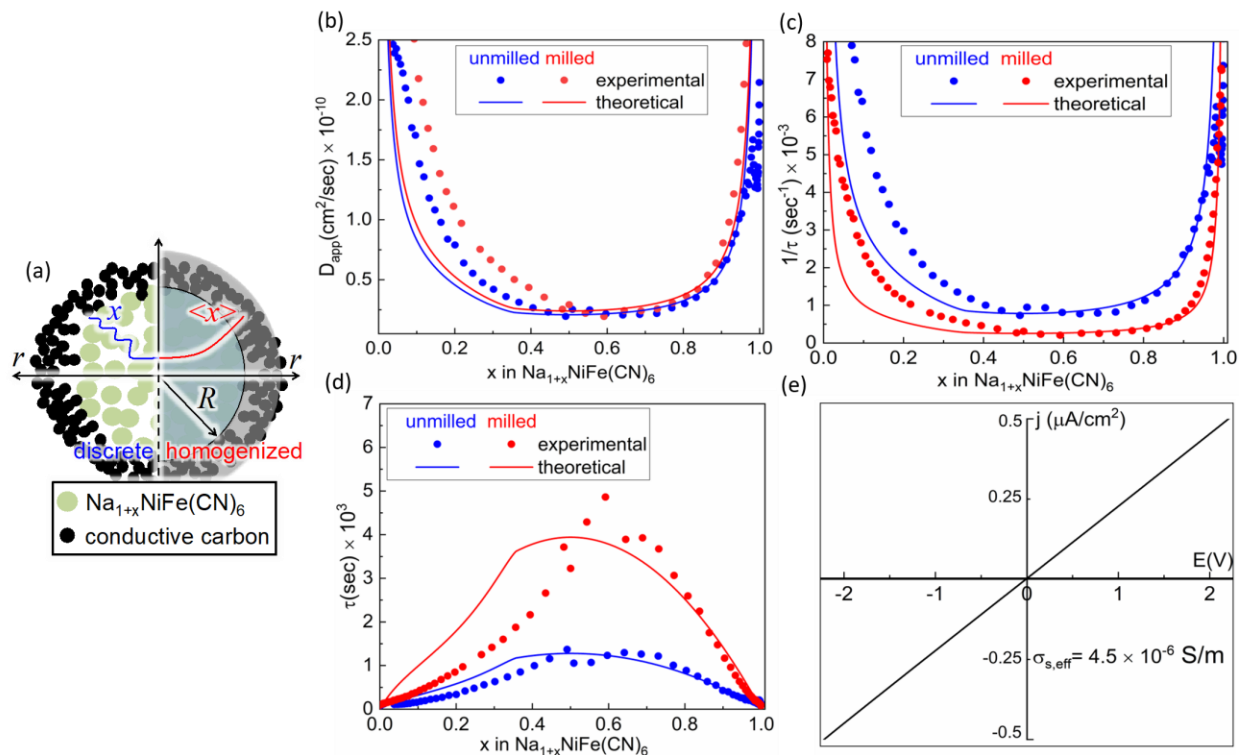


Figure 2.7: (a) Homogenized model of discrete nanoparticles in agglomerates, and (b) apparent diffusion coefficients theoretically predicted and as obtained from both electrodes, and (c-d) comparison of experimental and theoretical values of $1/\tau$ and τ versus the degree of intercalation. (e) Current-voltage response for measuring electronic conductivity of bulk NiHCFE powders at 0% SOC.

To predict the value of apparent diffusion coefficients using this theory we measured the effective electronic conductivity $\sigma_{s,eff}$ of as-synthesized NiHCFE NPs compacted into a pellet (see Experimental Methods). Fine particles with strong attractive interactions are known to aggregate into locally jammed structures.⁷⁶ Accordingly, our estimate for agglomerate conductivity based on a 50%-dense pressed NiHCFE pellet is an upper bound for the actual conductivity of agglomerates. Note that the use of carbon black and PVDF was omitted from these samples and that these measurements were performed absent of electrolyte, so as to eliminate conduction through carbon and electrolyte,

thereby isolating electronic conduction only through NiHCFE NPs. For the porous pellets having an NiHCFE volume fraction v_s of approximately 50% the observed current/voltage response was ohmic with an effective electronic conductivity equal to 4.5×10^{-6} S/m (Fig. 2.5(e)). Using this result together with $\partial\phi_{eq}/\partial x$ from the modified regular solution model, we predicted the apparent diffusion coefficient of Na^+ in NiHCFE agglomerates as a function of the DOI x (Fig. 2.5(b)).

Comparison of these theoretical findings with experimental measurements from PITT is somewhat challenging. While dynamic light scattering and laser diffraction measurements can be used to characterize the size distribution of primary particles, these techniques require dispersion of agglomerates in a liquid medium. This leads to inaccurate measurement of agglomerate sizes since they are embedded in a conductive matrix of carbon black in the electrodes. Therefore, we determine the particular agglomerate radius R_{best} that minimizes the sum of square errors between experimental and theorized $1/\tau$ values (equal to D_{app}/R^2). We subsequently rationalize these findings for fitted agglomerate radii based on SEM imagery and single particle galvanostatic cycling simulations.

Table 2.1 summarizes the parameters used in calculation of the theoretical $1/\tau$, and it shows the resulting fitted agglomerate radii values for both unmilled and milled electrodes. For a given agglomerate radius R our theory predicts $1/\tau = (\sigma_{s,eff}/R^2 q_{max})(-\partial\phi_{eq}/\partial x)$. To evaluate this expression, we used the $\sigma_{s,eff}$ and q_{max} values listed in Table 1 and used $\partial\phi_{eq}/\partial x$ from the modified regular solution model. q_{max} was calculated using the maximum charge capacities measured from galvanostatic cycling (68 mAh/g and 60 mAh/g for unmilled and milled electrodes respectively), the

agglomerate volume fraction of binder- and carbon-free pellets (approximately 50%), and a density of 1.8 g/cm^3 for NiHCF as calculated from X-Ray diffraction data assuming ideal stoichiometry. The best-fit agglomerate sizes ($2R_{best}$) for the unmilled and milled electrodes were $3.26 \text{ }\mu\text{m}$ and $6.14 \text{ }\mu\text{m}$, respectively. The ranges of agglomerate sizes shown in Table 2.1 were obtained by point-wise fitting of experimental $1/\tau$ to theory, the 95% confidence interval of which is shown in the table. These results indicate that the milled electrode has a wider distribution of agglomerate size compared to the unmilled electrode, a conclusion that is qualitatively corroborated by examination of the porous microstructure of the two electrode types (see Figs. 2.1(e,f)).

Experimental diffusion coefficients were calculated by multiplying $1/\tau$ with $(R_{best})^2$ to enable comparison with theoretical values. The minimum diffusion coefficient thus calculated for both the electrodes is $\sim 10^{-11} \text{ cm}^2/\text{s}$, which is of similar order to previous galvanostatic intermittent titration measurements⁷⁷ for NiHCF porous electrodes but is two orders smaller than that of NiHCF thin films.³⁸ The reduction in the apparent diffusivity of porous electrodes relative to thin films is likely attributable to grain boundaries and structural defects within NPs and porosity and contact resistance between agglomerated NPs. Figs. 2.7(c) and 2.7(d) show the resulting $1/\tau$ and τ values as a function of x for both theory and experiment. The diffusion time scales are within 20% of the theoretical prediction near $x \approx 0.5$. The deviation at all values of x most likely arises due to errors in the value of electronic conductivity used (since agglomerates can have different conductivity compared to the 50% dense pellet tested), the anisotropy of agglomerate shapes, and the polydispersity of agglomerate sizes. The larger errors

observed for the milled electrode are at least in part attributable to its wider distribution of agglomerate sizes relative to the unmilled electrode.

	Unmilled electrode	Milled electrode
$\sigma_{s,eff}$	$4.5 \times 10^{-6} \text{ S/m}$	$4.5 \times 10^{-6} \text{ S/m}$
q_{max}	$2.22 \times 10^8 \text{ C/m}^3$	$1.93 \times 10^8 \text{ C/m}^3$
agglomerate diameter, $2R$	1.6 to 5 μm	4 to 13 μm
minimum D_{app}	$1.71 \times 10^{-11} \text{ cm}^2/\text{s}$	$2.69 \times 10^{-11} \text{ cm}^2/\text{s}$

Table 2.1: Parameters used to calculate theoretical $1/\tau$ values and parameters obtained by fitting theoretical $1/\tau$ to experiment.

Nevertheless, the diffusion time scales obtained from this theory have proven accurate to within an order of magnitude when compared to experiment. Fig. 2.5(b) shows the apparent diffusion coefficient values obtained from experiment (assuming an agglomerate radius equal to R_{best} in both cases) and from theory using Eq. 2.5.

Further we validate our theory for apparent diffusion by simulating galvanostatic cycling using the theoretical diffusion coefficient ($D_{app,theory}$ obtained from Eq. 2.5) and using experimentally determined diffusion coefficient (assuming $D_{app,experiment} = (R_{best})^2/\tau$). Simulated predictions of utilization and polarization using both of these diffusion-coefficient datasets are shown for both electrode types in Figs. 2.8(a,b). These simulations assume fast interfacial kinetics and facile crystal scale diffusion to compute spatiotemporal concentration profiles in a spherical agglomerate subject to Na^+ conservation inside of a spherical electroactive phase cycled at a certain C-rate. We note

that this boundary value problem can be posed without knowledge of the particular radius of the electroactive sphere being modeled if the C-rate and $1/\tau$ values are specified (see Appendix A for a complete derivation demonstrating this point). Here, we explicitly include the effect of the concentration-dependent diffusion coefficient.

For the milled electrode, simulations using the two sources of D_{app} data produce practically the same utilization across the entire C-rate range. These simulations produce 60% utilization at a rate 1.5 times slower than experiment. For the unmilled electrode simulations, $D_{app,theory}$ produces 60% utilization at a 44% faster rate than $D_{app,experiment}$, and the experimentally measured utilization falls between the two. In contrast, simulated polarization from both D_{app} datasets of both electrode types deviates from experiment especially at high C-rates (Fig.2.8(b)). We attribute this discrepancy primarily to the effects of ohmic resistance and distributed reactions within the porous electrodes that are neglected in the simulations. Moreover, since the simulations only consider limitations due to diffusion within nanoparticle agglomerates, saturation of polarization is observed at higher C-rates. At higher currents, in the real electrode, other ohmic effects (such as the resistance of carbon matrix in which the agglomerates are embedded) start dominating the total polarization. These effects are not incorporated into the model, and hence the saturation of polarization from the simulations indicates the limited contribution of diffusion to the overall impedance at high currents. Nonetheless, this simplified model shows that the observed capacity variations with rate are primarily a result of the apparent cation diffusion processes characterized by PITT.

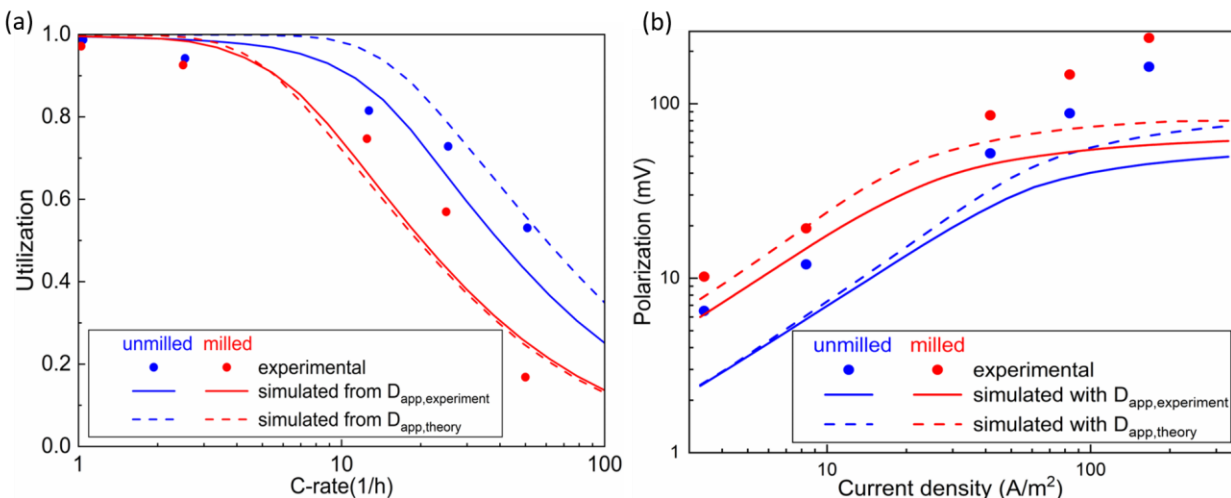


Figure 2.8: (a) Charge capacity utilization and (b) polarization versus current density compared between galvanostatic experimental data and the agglomerate scale diffusion model using D_{app} from experiment and theory.

2.5 Summary: Electron limited apparent diffusion

We characterized and developed theory for the apparent diffusion of cations within nickel hexacyanoferrate (NiHCF_e), an attractive candidate intercalation compound for applications in energy storage and water desalination. PITT experiments were conducted on porous NiHCF_e electrodes to determine the variation of apparent diffusion coefficient with the degree of intercalation (DOI). These measurements reveal that the diffusion coefficient is minimized near 50% degree-of-intercalation and is maximized at the terminal degrees-of-intercalation (i.e., 0% and 100%), thus varying by an order of magnitude from 10^{-11} cm²/sec to 10^{-10} cm²/sec during galvanostatic cycling. Further, to identify the effect of nanoparticle agglomeration on rate capability, two distinct electrode preparation procedures were used which resulted in different average agglomerate sizes in both electrodes. It is revealed that two-fold higher rate capability and three-fold faster diffusion time scales at 50% DOI are achievable when NP radius is reduced by two-fold. Simulations of galvanostatic cycling that include mass transfer resistance solely due to

the apparent diffusion effects probed with PITT show agreement with experimentally measured charge capacity utilization across a range of C-rates. These findings confirm that apparent diffusion phenomena limit galvanostatic rate capability. Furthermore, our new theory explains the profile of the apparent diffusion coefficients versus DOI reported from our PITT experiments. A simple expression is derived for the apparent diffusion coefficient that is proportional to the effective electronic conductivity, and that varies inversely with the volumetric differential charge capacitance for intercalation of Na^+ . Therefore, it follows that slow electronic conduction in NiHCFe agglomerates limits the rate capability of these electrodes, and these insights will enable development of future electrodes with high rate capability.

Although the diffusion coefficients from this theory show good agreement with experiments near 50% DOI, larger deviations are observed away from this range. These discrepancies likely arise due to the anisotropy of particle shapes, polydispersity of agglomerate sizes, and the inaccuracies in the measurement of agglomerate effective electronic conductivity. More focused physical characterization and modelling of electroactive particles is required to obtain higher accuracy in prediction of diffusion coefficients and hence rate capability. Specifically, other factors influencing rate capability include exchange current density of intercalation kinetics, contact resistance between conducting backbone and active material, and electron conduction through the carbon backbone itself. Also, the dependence of effective electronic conductivity on the degree of intercalation and agglomerate microstructure can be characterized. Experimental characterization techniques and advanced microscale models of porous electrodes should be employed to identify and quantify various sources of charge transfer

resistances that can limit rate capability of porous electrodes of NiHCF and other PBAs. Further, for electrodes of increased thickness, ionic transport limitations within electrolyte in the electrode pore space will affect performance in addition to apparent diffusion and kinetic processes.

Chapter 3 : Investigating divalent ion insertion mechanisms in Nickel hexacyanoferrate

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3.1 Understanding capacity fade with divalent ion intercalation in NiHCF_e

While NiHCF_e shows exceptional performance in monovalent electrolytes, this material has significant limitations when cycled with divalent cations. During galvanostatic cycling of NiHCF_e in $\text{Mg}^{2+}_{(\text{aq})}$ or $\text{Ca}^{2+}_{(\text{aq})}$, rapid capacity fade and poor rate capability is observed,⁶ whereas Mg^{2+} fails to intercalate into NiHCF_e and other PBAs from organic electrolytes.⁷⁸ The mechanism of capacity degradation and its partial retention in divalent aqueous electrolytes is not presently understood. Considering the significant concentration of Mg^{2+} and Ca^{2+} ions dissolved in saline water sources along with Na^+ (such as seawater) and their common presence as hardness in treated water, the mechanism of intercalation of Mg^{2+} and Ca^{2+} into NiHCF_e needs to be elucidated to develop stable, long-lasting faradaic deionization devices.

Although many studies have characterized the mechanisms of intercalation of monovalent ions, the same cannot be said for divalent ions such as Mg^{2+} and Ca^{2+} . It is well established that monovalent ions occupy body centered interstitial sites during intercalation into PBAs.^{4,79} Further, Li^+ and Na^+ have been shown to enter as hydrated ions whereas K^+ fully dehydrates before entering due to its large ionic radius.^{78,80,81} Important insights have also been gained on the role of anions in the electrolyte in the overall intercalation reaction,³⁴ and how the low electronic conductivity of PBAs can determine rate capability in porous electrodes cycled in $\text{Na}^+_{(\text{aq})}$.²³ In contrast, studies on

the intercalation of divalent ions have been limited.⁸ While some experimental evidence suggests that Mg^{2+} enters as a partially hydrated ion during cycling in aqueous electrolytes in a PBA,^{8,78} the crystal sites that it occupies have not been clearly identified. While the capacity fade of NiHCF_e in aqueous divalent electrolytes has been linked to the dissolution of Ni^{2+} ,⁶ the atomic and electronic mechanisms of this process have not been investigated.

Here, we perform an in-depth investigation for the intercalation of $\text{Mg}^{2+}_{(\text{aq})}$ and $\text{Ca}^{2+}_{(\text{aq})}$ in porous electrodes containing nickel hexacyanoferrate. Using experiments and first principles calculations, we analyze the degradation of NiHCF_e during (de)intercalation and explain the mechanism for the same. We show that Ni^{2+} ions in NiHCF_e can be partially substituted by Mg^{2+} or Ca^{2+} during galvanostatic cycling in aqueous electrolytes with these divalent ions. The difference in bonding of Ni and Mg with adjacent N atoms ultimately results in the dissolution of Ni^{2+} and $(\text{Fe}(\text{CN})_6)^{3-}$ ions into the surrounding water. $\text{Fe}(\text{CN})_6$ ions in the host can also be rendered inactive due to the inhibition of electron transfer through CN ligands bonded to Mg. The loss of $\text{Fe}(\text{CN})_6$ ions from the host structure through these mechanisms leads to capacity fade observed experimentally.

3.2 Experimental characterization of divalent ion intercalation in NiHCF_e

NiHCF_e and the corresponding porous electrodes were synthesized as described in section 2.2.1 and section 2.2.2 respectively. Considering the large interstitial sites present for cation intercalation in PBAs (~0.5 nm based on crystal structure) compared to the ionic radii of Mg^{2+} and Ca^{2+} , divalent ions would be expected to intercalate into NiHCF_e without disturbing its structure based on steric effects alone. However, Fig. 3.1(a) shows that when NiHCF_e is cycled in 1M MgCl_2 (aq) and CaCl_2 (aq), charge capacity

rapidly decreases to nearly 25 % of the initial capacity after 120 cycles, with coulombic efficiency between 97 and 100 %. Because the lattice parameters of analogous PBAs have been shown to vary by less than 1% during (de)intercalation of $\text{Mg}^{2+}_{(\text{aq})}$ ⁸² such capacity loss is likely not due to an irreversible change in crystal structure. To investigate the mechanism of capacity fade we further analyze cyclic voltammetry and galvanostatic cycling of NiHCF_e in $\text{Mg}^{2+}_{(\text{aq})}$.

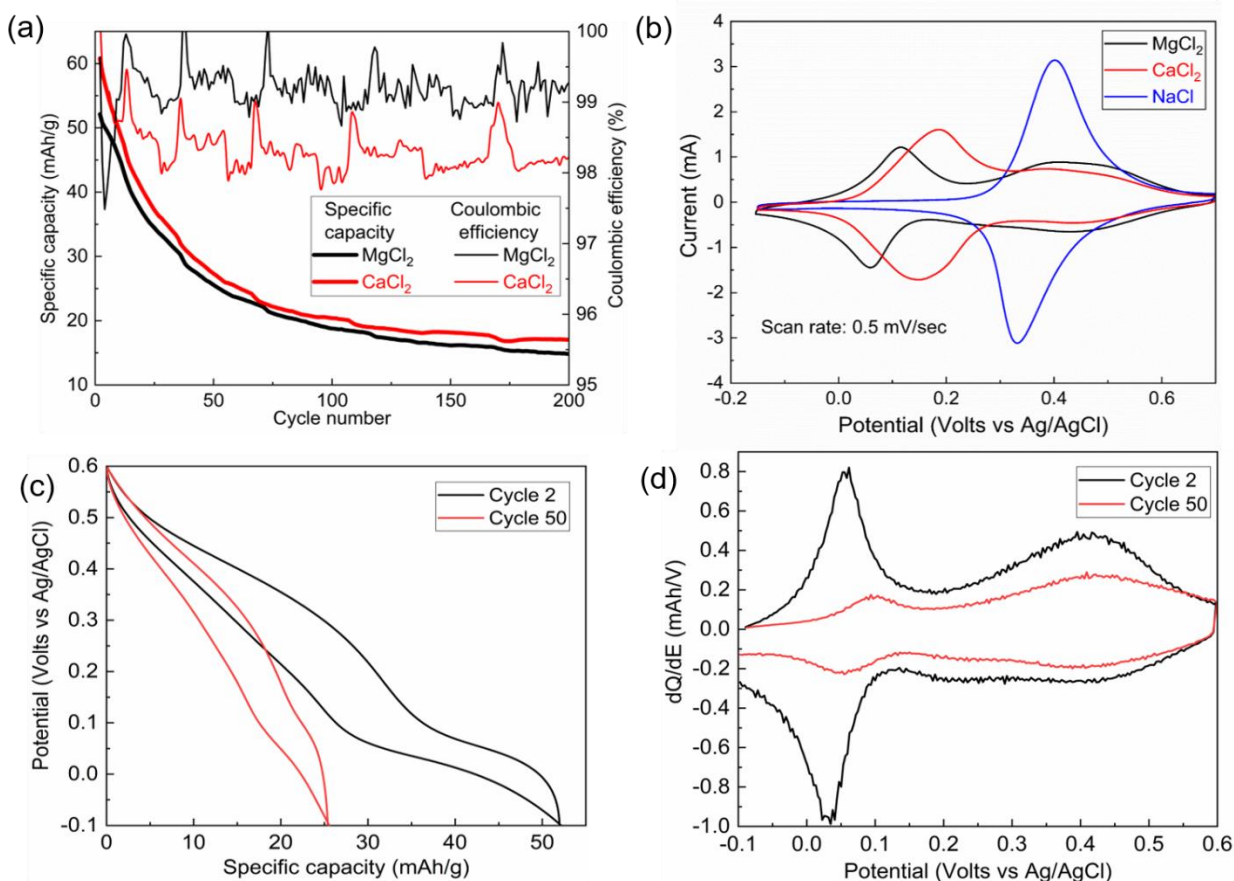


Figure 3.1:Galvanostatic cycling performance at 1C (a) and cyclic voltammetry plot at 0.5 mV/s (b) for NiHCF in 1M $\text{MgCl}_2(\text{aq})$ and $\text{CaCl}_2(\text{aq})$. Comparison of potential variation with specific capacity (c) and variation of differential capacitance (dQ/dE) with potential (d) for 2nd and 50th cycles during galvanostatic cycling of NiHCF_e in 1M $\text{MgCl}_2(\text{aq})$.

Cyclic voltammetry and dQ/dE measurements strongly suggest that there are two distinct modes for intercalation of divalent cations. Cyclic voltammetry shows two distinct peaks

separated by ~ 400 mV for both Mg^{2+} and Ca^{2+} (de)intercalation (Fig. 3.1(b)), indicating a more complex mechanism for intercalation of divalent ions compared to monovalent ions that show a single peak. The variation of potential (E) with specific capacity (Q) in Fig. 3.1(c) also shows two distinct redox regimes, unlike the case for Na^+ (aq) and K^+ (aq) intercalation where a single redox regime is seen (Fig. 3.1(b)).^{4,23} Two distinct peaks of differential capacitance (dQ/dE) are observed during the initial cycles (Fig. 3.1(d)) with potential separation similar to that observed in cyclic voltammetry. However, the peak at lower potential diminishes in intensity as the number of cycles increases: the ratio of intensity of the two peaks at 0.05 V and 0.45 V respectively changes from 1.68 in the 2nd cycle to 0.60 in the 50th cycle. Thus, the particular mode by which Mg is inserted into the host PBA at low potential is apparently less favored than the insertion mode at high potential as cycling progresses.

We also observed that the electrolyte in the flooded cell setup changes from being transparent to a light yellow color (Appendix C, Fig. C1(a)) as cycling progresses, indicating the release of $(\text{Fe}(\text{CN})_6)^{3-}$ ions during cycling. EDXRF experiments confirmed the presence of Fe and Ni ions in the MgCl_2 (aq) electrolyte when analyzed after 500 cycles (Table 3.1). Raman spectroscopy of the electrolyte post cycling (Fig. 3.2) reveals a distinct peak for the CN stretch mode at 2181 cm^{-1} , confirming Fe is present in the electrolyte as $(\text{Fe}(\text{CN})_6)^{3-}$.⁸³ Because such species were below the detection limits of EDXRF and Raman during initial cycles, we conclude that both Ni^{2+} and $(\text{Fe}(\text{CN})_6)^{3-}$ ions are released into the electrolyte during the intercalation of Mg^{2+} into NiHCFE. Moreover, the presence of Ni^{2+} in the electrolyte post cycling suggests that Mg^{2+} displaces Ni^{2+} from the host lattice when it inserts into the structure.

Element	Relative weight percent in electrolyte post
Fe	0.074 %
Ni	0.056 %
Mg	14.657 %
Cl	85.214 %

Table 3.1: EDXRF of 1M MgCl₂ electrolyte post cycling NiHCFe

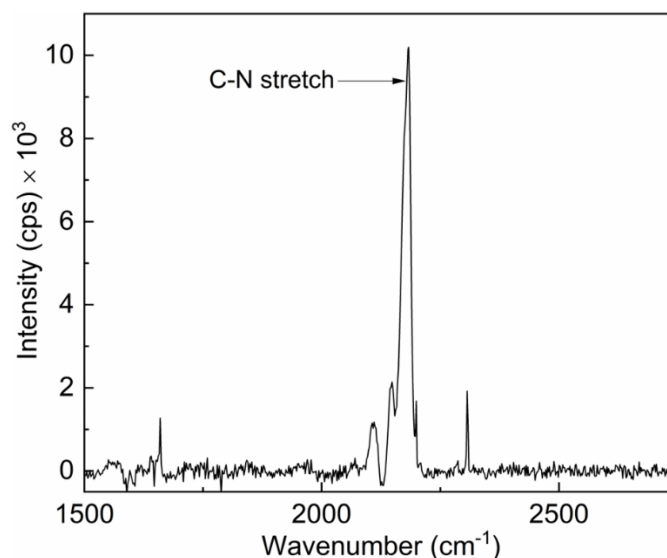


Figure 3.2: Surface enhanced Raman spectroscopy of 1M MgCl₂ (aq) electrolyte post galvanostatic cycling of NiHCFe for 500 cycles at 1C

Therefore, based on these experimental observations, we propose that Mg²⁺ can partially substitute Ni²⁺ ions in the PBA host lattice. The substitution of Ni²⁺ by Mg²⁺ is also plausible based on their similar ionic radii - Mg²⁺(72 pm) and Ni²⁺ (69 pm).⁸⁴ This substitution can also weaken the bonds between (Fe(CN)₆)³⁻ and the atoms to which it coordinates in the lattice, leading to the subsequent dissolution of (Fe(CN)₆)³⁻ when Ni²⁺ is substituted by Mg²⁺ in the host lattice.

The prevailing notion in most previous research is that alkali and alkaline-earth cations intercalate into interstitial sites of PBAs^{6–8,23,82,85,86}, while transition metals occupy lattice sites in the framework. To test whether Mg²⁺ can instead occupy lattice sites, we

attempted to synthesize MgHCFE (magnesium hexacyanoferrate) using simple coprecipitation reactions. When $\text{K}_3\text{Fe}(\text{CN})_6(\text{aq})$ was mixed with $\text{MgCl}_2(\text{aq})$, no reaction occurred irrespective of the duration of observation. However, a white precipitate formed when 0.1 M $\text{K}_4\text{Fe}(\text{CN})_6(\text{aq})$ was mixed with 0.2M of $\text{MgCl}_2(\text{aq})$ (Fig. 3.3(a)). Using EDXRF data for relative weight percentages of metal ions in this precipitate, a chemical formula was approximately calculated as $\text{K}_{1.75}\text{Mg}_{1.23}\text{Fe}(\text{CN})_6 \cdot y\text{H}_2\text{O}$, normalized to one Fe unit. XRD revealed a tetragonal structure with $a=10.10$ and $c=10.49$ (Fig. 3.3(c)). Such a structure was synthesized by Huggins and co-workers in 1977 with a nominal formula of $\text{K}_2\text{MgFe}^{\text{II}}(\text{CN})_6$ that is analogous to the widely studied transition metal based PBAs, $\text{K}_2\text{MFe}^{\text{II}}(\text{CN})_6$ ($\text{M} = \text{Fe}, \text{Cu}, \text{Ni}, \text{Co}, \text{and Mn}$).⁸⁷ In that previous work $\text{K}_2\text{CaFe}(\text{CN})_6$ (CaHCFE) was also found to have a tetragonal symmetry, similar to MgHCFE. This finding suggests that not only Mg^{2+} but even large ions such as Ca^{2+} can stably reside in the host lattice of PBAs at room temperature and that Ca^{2+} intercalation likely follows a similar mechanism to Mg^{2+} . Moreover, since no reaction occurs when using $(\text{Fe}(\text{CN})_6)^{3-}$ ions (i.e., instead of $(\text{Fe}(\text{CN})_6)^{4-}$), the oxidized form of this compound is apparently highly soluble in water.

We tested the electrochemical activity of MgHCFE(s) in 1M $\text{MgCl}_2(\text{aq})$ using a flooded cell setup. During the oxidation step of the first cycle, nearly all capacity was lost (Fig. 3.3(d)) and the electrolyte turned yellow (Appendix C, Fig. C1(b)), indicating immediate release of $(\text{Fe}(\text{CN})_6)^{3-}$ ions. This phenomenon is consistent with our finding that the oxidized form of MgHCFE (likely $\text{Mg}_{1.5}\text{Fe}^{\text{III}}(\text{CN})_6$) is soluble in water. Thus, these experiments establish that the presence of Mg^{2+} ions in lattice sites of the framework can lead to dissolution of active material during galvanostatic cycling. The immediate capacity loss and the onset

of electrochemical inactivity of MgHCFE can be attributed to the high solubility of the $\text{Mg}_{1.5}\text{Fe}^{\text{III}}(\text{CN})_6$ phase in water. The solubility of this hypothetical compound could result from weak Mg-N bonding in the lattice arising from the lack of pII-dII bonding between Mg and N that is otherwise present between transition metal centers and N in other PBAs.⁸⁷

Next, we tested whether Ni^{2+} and Mg^{2+} can coexist in the lattice framework and whether such a material can cycle reversibly at constant current. To do this we performed a simple ion-exchange reaction by dispersing MgHCFE powder in 0.5M NiCl_2 for >2 weeks. The particles obtained after thorough cleaning changed color from white to green (Fig. 3.3 (b)) with a hue similar to $\text{K}_2\text{NiFe}(\text{CN})_6$. This observation indicates that Ni^{2+} ions occupy the lattice sites in the framework by substituting Mg^{2+} , at least partially. EDXRF reveals a formula of $\text{K}_{1.21}\text{Mg}_{0.57}\text{Ni}_{0.64}\text{Fe}(\text{CN})_6 \cdot x\text{H}_2\text{O}$, normalized to one Fe unit. Further, no Cl^- ions were detected, indicating there was no contamination from NiCl_2 that could have been responsible for the green hue observed. Thus, we denote these ion-exchanged powders as $\text{Mg}_x\text{Ni}_y\text{Fe}(\text{CN})_6$. XRD of $\text{Mg}_x\text{Ni}_y\text{HCFE}$ reveals a tetragonal structure with the same lattice parameter as MgHCFE (Fig. 3.3(c)). A phase transition of $\text{Mg}_x\text{Ni}_y\text{HCFE}$ to the cubic Fm-3m structure of NiHCFE was not observed, likely due to the significant amount of Mg still present in the lattice framework. However, a stark contrast in the galvanostatic cycling is observed when it is cycled in 1M $\text{MgCl}_{2(\text{aq})}$. Unlike MgHCFE which essentially loses all of its capacity during the first cycle due to dissolution of the $\text{Mg}_{1.5}\text{Fe}^{\text{III}}(\text{CN})_6$ phase, $\text{Mg}_x\text{Ni}_y\text{HCFE}$ releases $\text{Fe}(\text{CN})_6^{3-}$ ions at a much slower rate and its capacity stabilizes to nearly 15 mAh/g after 70 cycles (Fig. 3.3(d)). This capacity is within 5% of the capacity of NiHCFE after cycling for 200 cycles in 1M $\text{MgCl}_{2(\text{aq})}$ (Fig. 3.1(a)).

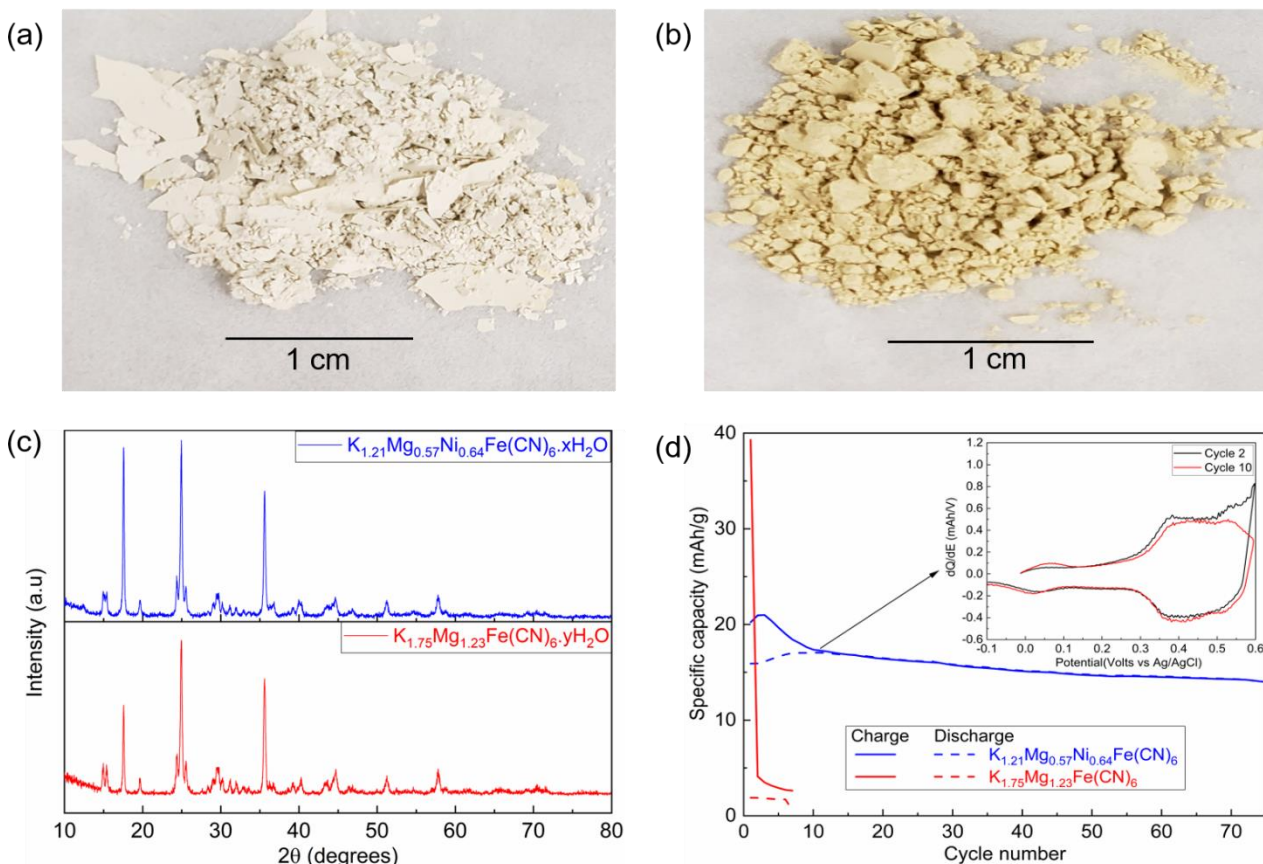


Figure 3.3: (a) White powders of MgHCFE and (b) green Mg_xNi_yHCFE powders obtained after ion exchange reaction of MgHCFE in $NiCl_{2(aq)}$. (c) X-ray diffraction patterns of MgHCFE and Mg_xNi_yHCFE powders and (d) galvanostatic cycling performance of porous electrodes made from these powders tested in 1M $MgCl_{2(aq)}$ electrolyte at 0.4 mA/cm^2 .

Therefore, these experiments establish that a stable PBA phase can be cycled with both Mg and Ni coexisting in the host structure. Moreover, while the presence of Ni^{2+} in the lattice framework enhances electrochemical stability, Mg^{2+} in the lattice framework leads to degradation and capacity loss due to dissolution of $Mg_{1.5}Fe^{III}(CN)_6$ in water. Based on these experimental findings, Fig. 3.4 shows the proposed reaction mechanism for (de)intercalation of $Mg^{2+}_{(aq)}$ into $NiHCFE$ in pure $MgCl_{2(aq)}$.

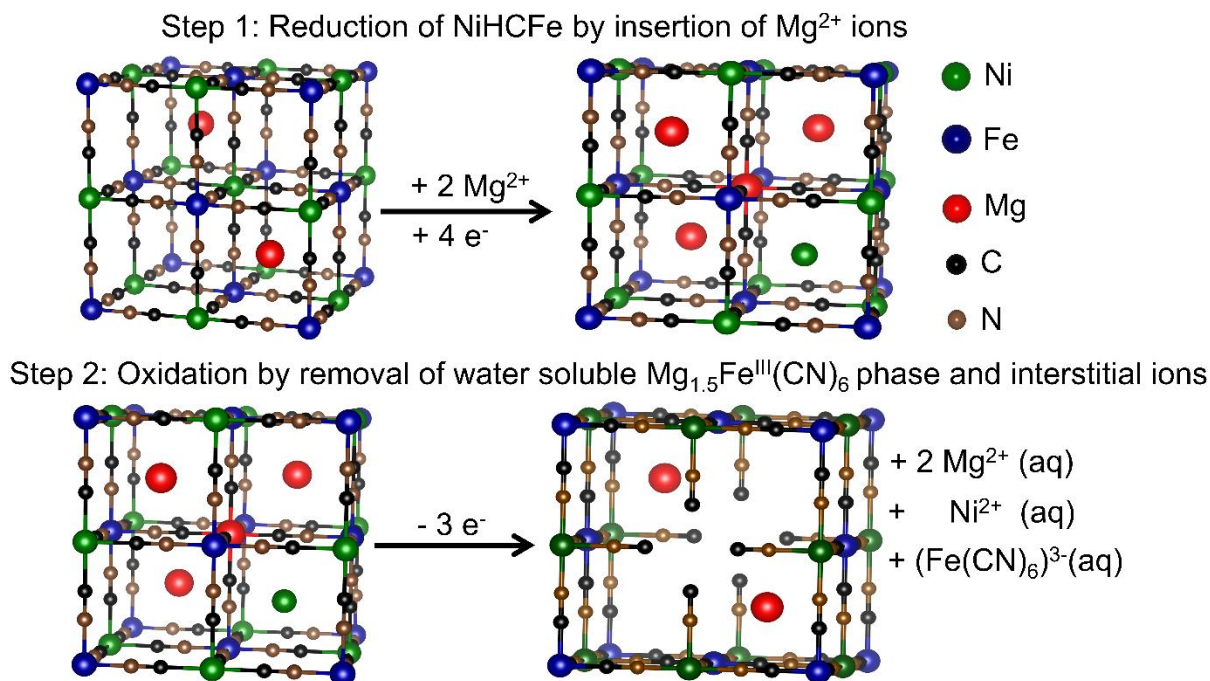


Figure 3.4: Proposed reaction mechanism of Mg^{2+} (de)intercalation that leads to degradation of NiHCFE during galvanostatic cycling in $\text{Mg}^{2+}_{(\text{aq})}$. Note that Mg^{2+} ions maybe partially hydrated, but water molecules are omitted for clarity and simplicity.

To identify the redox regimes for intercalation of Mg^{2+} into the two different sites proposed in the reaction mechanism (i.e., interstitial sites and Ni^{2+} site in the lattice framework) we further analyzed the variation of dQ/dE with potential for $\text{Mg}_x\text{Ni}_y\text{HCFE}$ (inset Fig. 3.3(d)) during its galvanostatic cycling in $1\text{M } \text{MgCl}_{2(\text{aq})}$. The low potential peak (at 0.05V) is negligible compared to the high potential peak (at 0.45V). The same trend is observed in the variation of dQ/dE with potential for NiHCFE, albeit after the first 100 cycles. Since $\text{Mg}_x\text{Ni}_y\text{HCFE}$ already has significant amount of Mg^{2+} ions present in the lattice framework, we expect the majority of $\text{Mg}^{2+}_{(\text{aq})}$ to intercalate into interstitial sites rather than substituting Ni^{2+} in the lattice framework. Similarly, during intercalation into NiHCFE, we expect Mg^{2+} to occupy interstitial sites after degradation of the structure due to the dissolution of Ni^{2+} and $\text{Fe}(\text{CN})_6^{3-}$ during initial cycling. Therefore, the peak of dQ/dE at 0.45V in both compounds likely corresponds to the intercalation of Mg^{2+} into interstitial sites, and hence

the substitution of Ni^{2+} by Mg^{2+} occurs in the low potential regime. Hence, we deduce that intercalation of Mg^{2+} ions into interstitial sites results in the retention of capacity, whereas displacement of Ni^{2+} in the lattice framework by Mg^{2+} ions is responsible for the observed capacity fade.

3.3 First principles calculations for divalent intercalation in NiHCF

Guided by the experimental evidence that the capacity fade experienced by NiHCF is linked to the substitution of Ni^{2+} in the framework by $\text{Mg}^{2+}/\text{Ca}^{2+}$, we used first principles simulations to identify the atomic and electronic effects that affect substitution and to deduce the implications of substitution on electron density distributions and electron transfer within PBAs. We performed DFT calculations on two different supercells of $[\text{MgNiFe}(\text{CN})_6]_4$: (1) a “pristine” configuration with all Mg^{2+} ions in interstitial sites and all Ni^{2+} ions in the lattice framework and (2) a “swapped” configuration where one interstitial Mg^{2+} ion is exchanged with one Ni^{2+} ion in the lattice framework (Fig. 3.5).

3.3.1 Density functional theory calculations

Density functional theory (DFT) calculations were performed with collinear-polarized spin using the Quantum ESPRESSO (QE) package.⁸⁸ Correlation interactions were modelled using the generalized gradient approximation with the Perdew–Burke–Ernzerhof (PBE) functional and Hubbard corrections (GGA +U).^{89–91} The U values for Ni and Fe were taken to be 3 eV and 1 eV respectively,^{92,93} to stabilize the high-spin/low-spin ground state. The valence electrons for Ni, Fe, and Mg atoms corresponded to $3d^9 4s^1$, $3d^7 4s^1$, and $2s^2 2p^6 3s^2 3p^0$, whereas the remaining electrons were kept frozen as core states. Scalar-relativistic Ultrasoft pseudopotentials were employed to describe the interaction between valence and frozen electrons. A cutoff energy of 2040 eV was used in all cases

for the truncation of plane-wave basis sets. Monkhorst–Pack k -points were used in every calculation with a $4\times4\times4$ grid for the $2\times2\times2$ supercell, producing a real space cutoff of $0.136 \text{ \AA}$.⁹⁴ Charge density was smeared in each relaxation calculation using gaussian smearing scheme. Internal relaxation calculations were performed by relaxing atomic coordinates while fixing supercell symmetry as Fm-3m, in accordance with experimental X-ray diffraction data.^{23,85} The lattice constant for each configuration was varied until a final pressure less than 0.1 kbar was obtained, while retaining the cubic symmetry of the supercell. Charge density obtained from self-consistent field calculations post internal relaxation were visualized using the VESTA open source software.⁹⁵

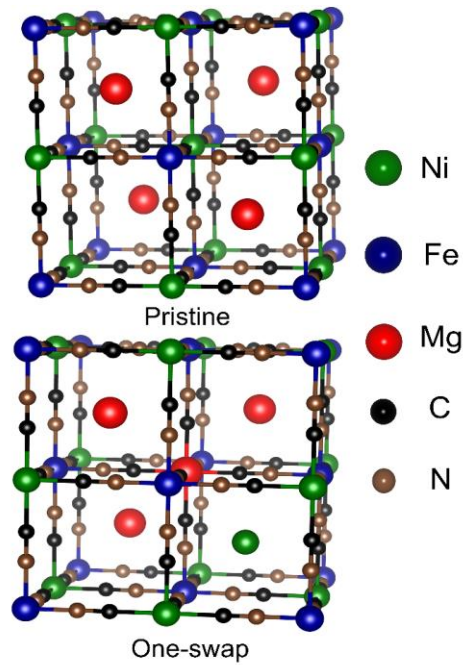


Figure 3.5: Pristine and one-swap configurations simulated in DFT calculations

3.3.2 Insights from DFT studies

As alluded to earlier, the site occupation of Mg^{2+} ions within PBAs is not well established in previous literature. If Mg^{2+} ions completely desolvate before entering the PBA host, the 24d (face-centered) interstitial site is energetically favored over the 8c (body-centered) interstitial site that Na^+ and K^+ occupy.^{86,92} However, in aqueous electrolytes, Mg^{2+} has a large hydrated ionic radius of 0.8 nm⁹⁶ compared to the interstitial space available in PBAs (0.5 nm). Experimental studies suggest that Mg^{2+} enters at least partially hydrated.⁷⁸ Further, Na^+ has a hydrated ionic radius of 0.45 nm,⁹⁶ and it enters the PBA in the hydrated form to occupy the body center site.^{78,81} Given that $\text{Mg}^{2+}_{(\text{aq})}$ ions are much bigger than $\text{Na}^+_{(\text{aq})}$ ions, it is expected that the size of partially dehydrated $\text{Mg}^{2+}_{(\text{aq})}$ ions that enter the PBA will be similar to $\text{Na}^+_{(\text{aq})}$ ions after Mg^{2+} partly sheds its hydration shell. This logic suggests that Mg^{2+} ions will prefer body-centered occupancy in aqueous systems. Therefore, in the simulations, Mg^{2+} ions were placed at body center (8c) locations instead of face centered sites (24d). However, H_2O molecules were excluded from the simulations, and Mg^{2+} occupation is fixed at the body center to account for the steric effects of water molecules which constrain Mg^{2+} ions at body center locations in the real crystal. The remaining atoms were not constrained during structural relaxation. For $\text{MgNiFe}(\text{CN})_6$ there are twice as many body-centered interstitial sites as Mg^{2+} ions, and hence there are many possible ways to arrange Mg^{2+} ions in those sites. Recently, it was shown that configurations that have no nearest neighbor vacancies in body-centered sites minimize energy among all possible configurations.⁸⁶ Accordingly, $\text{MgNiFe}(\text{CN})_6$ was simulated without interstitial vacancy pairs. In the swapped configuration, Ni^{2+} ion at body center was swapped with the nearest Mg^{2+} ion. In doing so, it is assumed that water

molecules will redistribute to hydrate Ni^{2+} enabling Mg^{2+} to occupy the site that Ni^{2+} originally occupied.

The pristine and swapped configurations converged with lattice parameters of 10.19 Å and 10.24 Å at final pressures of 0.03 and 0.01 kbar, respectively. Table 3.2 shows that the energy difference between swapped and pristine configurations is small ($0.14 \text{ eV} = 5.6 kT$). The similarity of total energy between these two configurations suggests that some Mg^{2+} ions can substitute Ni^{2+} ions in the host lattice, leading to an increase in the overall entropy of the system at finite temperatures without a large energetic cost.

Energy difference contribution	Energy difference ($E_{\text{one-swap}} - E_{\text{pristine}}$) (eV)
Kinetic energy	-112.39
Exchange correlation	- 4.92
Electrostatic energy	117.74
Hubbard energy	0.05
Smearing contribution	- 0.07
Total Energy difference	0.14

Table 3.2: Comparison of energy difference contributions between pristine and one-swap configuration

To complement these DFT predictions, a simple statistical mechanical model was created to estimate the degree of substitution of Ni by Mg based on the value of the energy difference for a single swapping event, $\Delta E = E_{\text{one-swap}} - E_{\text{pristine}}$. Since the variation in lattice parameter between the two relaxed structures is less than 0.5% and the final pressure at the end of the internal relaxation calculations was close to zero, a canonical ensemble was analyzed with constant number N , volume V , and temperature T . This approach is also justified from ex-situ XRD data taken on NiHCFE electrodes during

cycling, where no appreciable change in lattice constant was observed even after hundreds of cycles. This observation indicates that the volume remains approximately constant throughout the intercalation process (Appendix C, FigC2). Additionally, it is assumed that the energy difference for multiple exchanges of Ni by Mg is an integer multiple of that obtained from DFT calculations for a single swap. Based on this analysis the fraction of Ni^{2+} ions (X_{swap}) that can be substituted by Mg^{2+} as a function of $\Delta E/kT$ (Fig. 3.6) was obtained. The detailed equations and explanation for these calculations are provided in the Appendix.

Fig. 3.6 shows that around 5% of Ni^{2+} ions can be substituted by Mg^{2+} ($X_{\text{swap}} \approx 0.05$) for $\Delta E = 5.6kT$ obtained from DFT. The variation of differential capacity with cycle number (Fig. 3.1(d)) suggests that these substitutions will occur during every cycle, although the tendency of Mg^{2+} to displace Ni^{2+} ions is expected to decrease with progressing cycle number, as already discussed for Figs. 3.1(a) and 3.1(d). Capacity fade data from experiments (Fig.3.1(a)) shows that 1.5 to 3% of the total charge capacity is lost per cycle in the first few cycles at a C-rate of 1C. If this loss in capacity is purely attributed to the substitution of host Ni^{2+} ions by Mg^{2+} , approximately 1.5% to 3% of Ni^{2+} are substituted by Mg^{2+} ions per cycle. The prediction of 5% substitution of Ni^{2+} by Mg^{2+} at equilibrium is similar in magnitude to the capacity loss per cycle, suggesting that swapping and subsequent dissolution could be responsible for the observed capacity fade rate. We note, however, that intercalated ion hydration, H_2O molecules in the PBA crystal, and $\text{Fe}(\text{CN})_6^{4-/3-}$ vacancies could affect the energy difference between these two configurations and X_{swap} . Because the hydration enthalpy of Ni^{2+} is lower than that of Mg^{2+} in bulk H_2O ,⁹⁷ the energy difference between the pristine and swapped

configurations is likely to further decrease, leading to an increase in the fraction of Ni substituted by Mg.

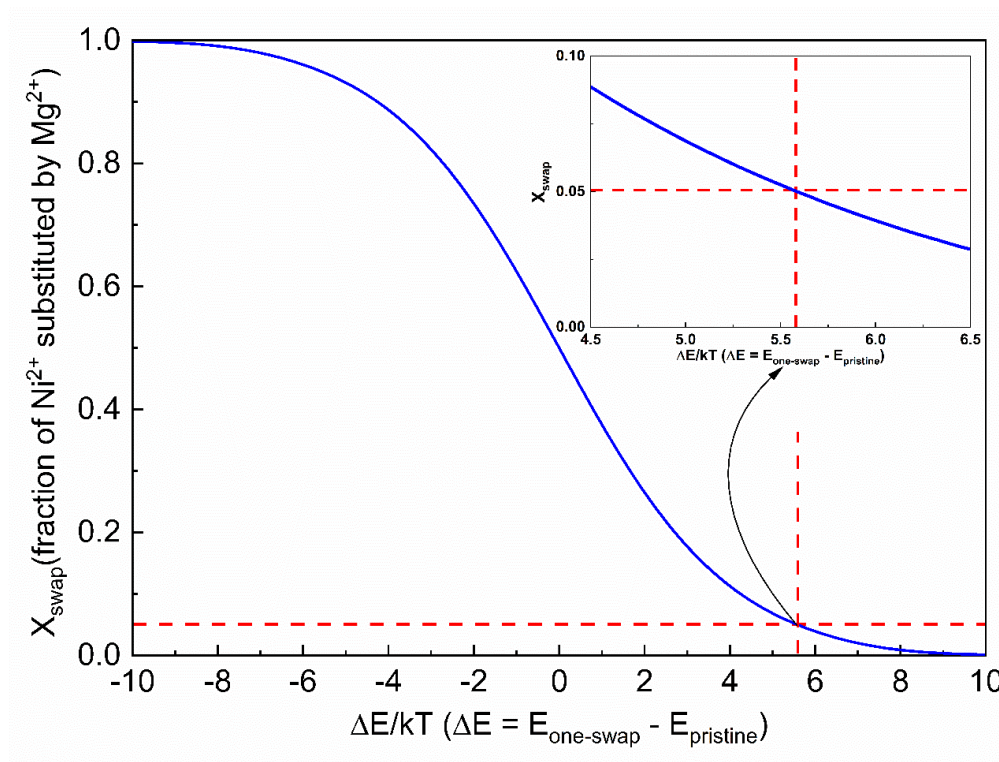


Figure 3.6: Fraction of Ni^{2+} ions that can be substituted by Mg^{2+} (X_{swap}) as a function of energy difference between swapped and pristine configurations.

The electronic density distributions and density of states (DOS) for both $\text{MgNiFe}(\text{CN})_6$ structures in addition to MgHCFe were also analyzed. Internal relaxation calculations of $\text{K}_2\text{MgFe}(\text{CN})_6$ resulted in a cubic structure with lattice constant of $10.4 \text{ \AA}$, at a final pressure of 0.08 kbar . Note that XRD of MgHCFe established its structure to be tetragonal with lattice parameters of $10.1 \text{ \AA}$ and $10.49 \text{ \AA}$. This peculiar asymmetry most likely arises due to presence of H_2O molecules and defects in the crystal structure, which are not simulated in the present DFT simulations. Nevertheless, we gain important insights with the DFT calculations of the MgHCFe structure by analyzing and comparing

its electronic structure with the pristine and swapped configurations of Mg-intercalated NiHCFE.

Figs. 3.7(a), 3.7(b) and 3.7(c) show that the electronic density distributions for these three structures differ mostly near the M atom in the CN-M-NC chain. The pristine NiHCFE structure has ~40% higher charge density at the midpoint of the Ni-N bond compared to the Mg-N bond in the one-swap and MgHCFE cases. The total density of states reveals a half-metallic character for both the pristine and one-swap structures while MgHCFE as an insulator (Appendix 3, A3.4). This finding was verified experimentally by performing IV measurements on dry compacted powders without carbon black. NiHCFE shows ohmic behavior, while MgHCFE shows insulating behavior (Appendix C, Fig. C5). However, the local density of states (LDOS) at M atom in the CN-M-NC chain presents a more interesting picture. LDOS near the Fermi energy (ε_f) for the outermost orbital of Ni in the pristine structure is an order of magnitude higher than in the one-swap case, whereas the LDOS at or near ε_f for Mg in MgHCFE is practically zero (Figs. 3.7(d), (e) and (f)). This stark contrast in LDOS suggests that Mg atoms present in the lattice framework act as insulating defects.

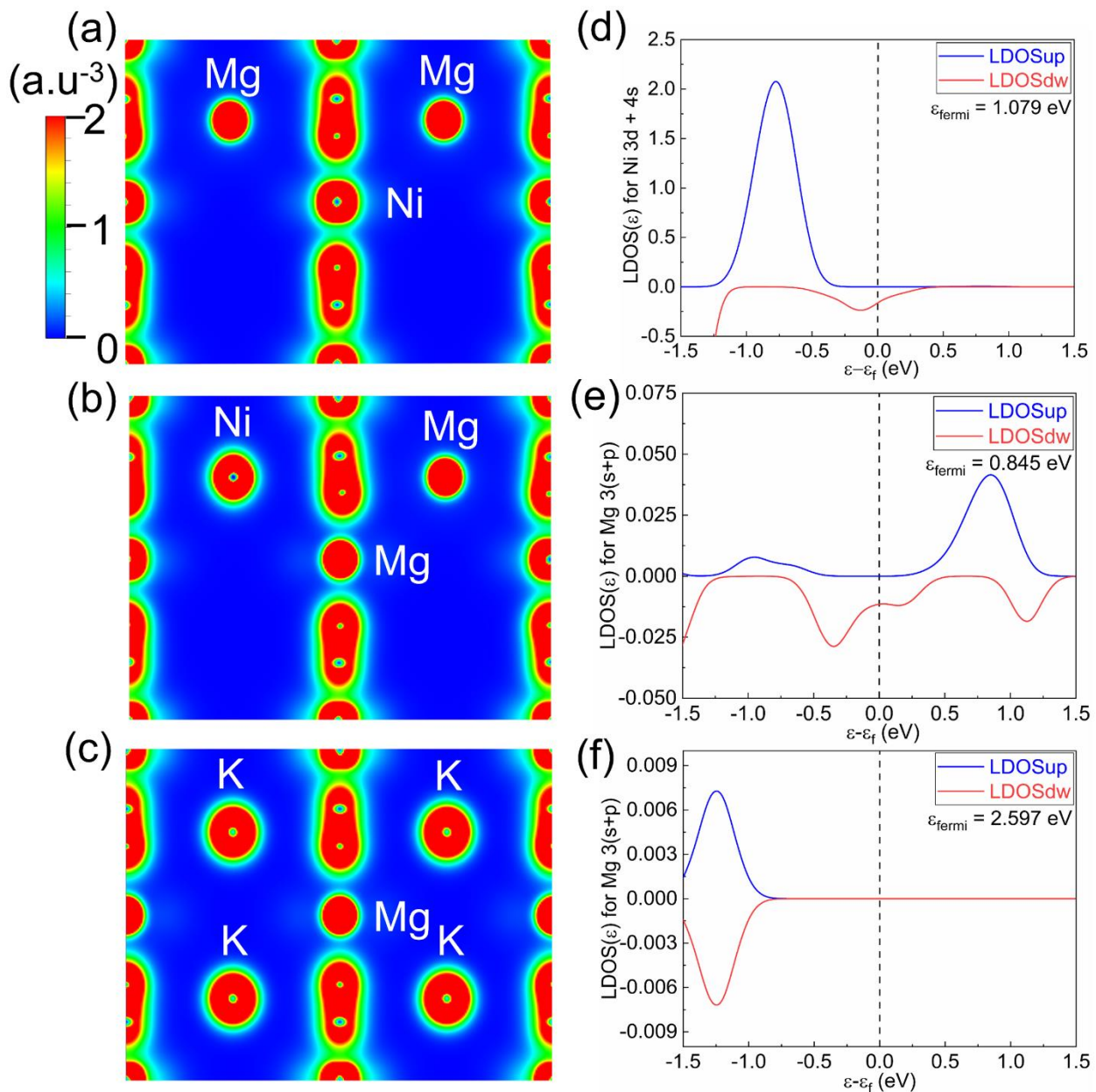


Figure 3.7: Electron density distributions for (a) pristine, (b) one-swap and (c) MgHCFE configurations in the 10-1 plane. Corresponding local density of states (LDOS (E)) vs energy (E) at the central metal atoms, i.e., Ni in the pristine configuration and Mg in one-swap and MgHCFE structures are plotted in (d), (e) and (f) respectively, with dashed lines corresponding to $\epsilon = \epsilon_f$ (fermi energy).

As a result of the insulating character of Mg in the lattice framework the redox of $\text{Fe}(\text{CN})_6^{3-}$ ions may be inhibited when CN ligands are bound to Mg. Moreover, electrons will be much more mobile in the pristine structure compared to the one-swap case due to

increased delocalization throughout the structure. This delocalization of electrons may also explain their lower kinetic energy as calculated in the one-swap structure compared to the pristine case (Table 3.2). Further, the increased electron density distribution around Ni atoms in the lattice framework (pristine case, Fig. 3.7(a)) relative to that around Mg atoms in the lattice framework (one-swap case, Fig. 3.7(b)) could be responsible for the decreased electrostatic energy of the pristine configuration relative to the one-swap configuration (Table 3.2). The lack of electrostatic interaction between Mg in the lattice framework and N was attributed to the absence of a pII - dII bond in Mg and Ca based PBAs.⁸⁷ Here we present the first quantitative evidence of this interaction based on electronic structure calculations.

Apart from the weakening of ferricyanide bonds that can result in their dissolution during oxidation, the presence of Mg^{2+} ions as insulating defects in the lattice framework may render some Fe ions electrically inactive. If the degree of substitution of Ni by Mg in the NiHCFe lattice is large enough, the insulating Mg centers can surround certain Fe ions and obstruct the transfer of electrons. This effect likely contributes to the capacity fade observed during intercalation of $\text{Mg}^{2+}_{(\text{aq})}$, together with the dissolution of $(\text{Fe}(\text{CN})_6)^{3-}$. To understand how the overall capacity may be affected because of Fe atoms being rendered inactive due to this effect, we created a lattice model for the percolation of electron transfer in the 3D lattice framework of NiHCFe. This model is comprised of a set of nodes, labeled either as Fe or Ni atoms, that are connected by electron-transferring ligands. We randomly substituted Ni atoms by Mg atoms in the lattice framework to produce a certain X_{swap} . If an Fe node becomes electrically isolated from an electron-percolating “backbone”, we deem it as electrically inactive, and hence such Fe nodes do

not contribute to charge capacity. Only those Fe ions connected to the electron-percolating backbone are considered redox active.

Fig. 3.8 shows the predicted capacity as a function of X_{swap} , obtained after ten random substitutions at each X_{swap} . 2D cross-sections of the PBA framework are shown at swapping fractions of 20%, 40%, 60%, 80% and 90%. At low values of X_{swap} , even though few Mg atoms substitute Ni, all nodes are “electrically connected” (shown in red), resulting in 100% charge capacity. However, at large X_{swap} (e.g., 90%), all Fe ions are electrically inactive (shown in blue), producing 0% charge capacity. This model partially explains the low initial charge capacity (~ 20 mAh/g) obtained for the MgHCF_e powders ion exchanged with Ni²⁺ (Mg_xNi_yHCF_e, Fig. 5). Since there is a significant fraction of Mg²⁺ ions in the lattice framework in these powders, many Fe ions may be rendered inactive, leading to a low initial capacity before degradation begins by ferricyanide dissolution.

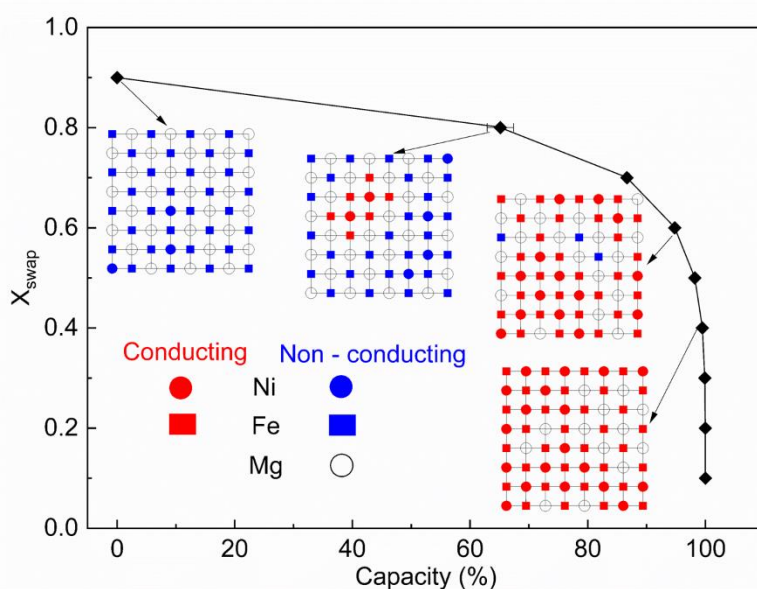


Figure 3.8: Predicting variation of capacity as a function of fraction of substitutions of Ni by Mg in a simplified model approximating the PBA framework as a resistive network.

Therefore, based on first principles calculations, it can be seen that the substitution of Mg^{2+} ions into Ni^{2+} sites in the PBA lattice framework is thermodynamically feasible. The capacity degradation of NiHCFE during galvanostatic cycling with $\text{Mg}^{2+}_{(\text{aq})}$ and $\text{Ca}^{2+}_{(\text{aq})}$ takes place due to loss of electroactive $\text{Fe}^{2+/3+}$ ions from the structure majorly due to dissolution of $(\text{Fe}(\text{CN})_6)^{3-}_{(\text{aq})}$. Capacity loss can further occur as a result of electrically-inaccessible Fe ions that become isolated by the presence of adjacent Mg^{2+} ions that act as insulating defects in the lattice framework.

3.3 Summarizing mechanistic insights of divalent ion intercalation in NiHCFE

We performed electrochemical characterization of nickel hexacyanoferrate (NiHCFE) electrodes in divalent aqueous electrolytes containing either Mg^{2+} or Ca^{2+} to analyze the degradation of NiHCFE during (de)intercalation of these ions. Cyclic voltammetry and differential capacity measurements suggest a two-site intercalation mechanism, whereas elemental analysis and Raman spectroscopy of the electrolyte post cycling revealed the presence of $\text{Fe}(\text{CN})_6^{3-}$ and Ni^{2+} ions. Using simple coprecipitation reactions, we showed that Mg^{2+} ions can reside in the host structure of a PBA in its reduced form. We observed that oxidation of either MgHCFE or $\text{Mg}_x\text{Ni}_y\text{HCFE}$ in $\text{MgCl}_{2(\text{aq})}$ will result in the release of $\text{Fe}(\text{CN})_6^{3-}$. Using first principles calculations, we showed that substitution of Mg into the host sites of NiHCFE is thermodynamically possible, and a simple statistical mechanics model can be used to estimate the degree of substitution of Ni^{2+} by Mg^{2+} . Moreover, based on electron density distributions and local density of states, we showed that if Mg^{2+} resides in the lattice framework of a PBA, it can act as an insulating defect, obstructing the transfer of electrons through CN ligands. A simple network theory of electron transfer predicts capacity loss due to the Fe ions resulting from insulating Mg defects on Ni sites.

Therefore, we have shown that divalent ions such as Mg^{2+} or Ca^{2+} have a tendency to displace Ni^{2+} from the host lattice in NiHCFE, apart from residing in the interstitial sites during the intercalation process, that subsequently leads to the degradation of charge capacity and the release of Ni^{2+} and $\text{Fe}(\text{CN})_6^{3-}$ ions from the host structure into the electrolyte.

Future work can delve into experimentally probing the positions of Mg^{2+} ions into the lattice framework of NiHCFE during intercalation from aqueous electrolytes using techniques such as chemical state analysis from X-ray photoelectron spectroscopy (XPS), nuclear magnetic resonance (NMR) and X-ray absorption near edge spectroscopy (XANES), although the poor activity of Mg^{2+} in some of these techniques could challenge such studies. Further, the kinetics of intercalation, the rate of diffusion of intercalating divalent ions and hydration of these ions could all impact the substitution of Ni^{2+} , which should be addressed in future studies to develop a more complete picture of the intercalation mechanism of divalent ions into PBAs.

Chapter 4 : NASICON materials for faradaic deionization

4.1: Need for selective separation of Na^+ over other cations in aqueous electrolytes

As discussed from previous studies on PBAs,^{98,99} while NiHCF_e shows modest charge capacity (~ 60 mAh/g at 1C) and long cycle life in monovalent electrolytes with Na^+ or K^+ , it degrades substantially in electrolytes with divalent ions (Mg^{2+} or Ca^{2+}).

In contrast to desalination of saline water, which motivates removal of all kinds of cations from the feed stream, there are several important applications where selective removal of certain ions is preferred over others. For instance, agriculture in saline regions faces an acute problem of ‘macronutrient poisoning’, wherein excess Na^+ (micronutrient for plants) competes with K^+ (macronutrient) and other ions (Mg^{2+} , Ca^{2+}) during water uptake by plants.^{100,101} This uptake of excess Na^+ instead of K^+ and other cations can significantly hamper the growth of plants and have adverse effects on the final produce. An FDI device using NiHCF_e has been attempted to demonstrate prevention of such a scenario, and successfully shown to selectively intercalate Na^+ over Mg^{2+} and Ca^{2+} .¹⁰² However, NiHCF_e has a 10:1 selectivity of K^+ over Na^+ ³ and hence cannot be effectively used to treat saline soils requiring the reverse order of selectivity (i.e., Na^+ over K^+). Further, the degradation of NiHCF_e due to Mg^{2+} and/or Ca^{2+} poses a challenge to the long-term life of such a system. Along with agriculture, there are many industrial separation processes such as purification of potassium-based salts^{20,103} which require highly selective removal of Na^+ over other alkali and alkaline earth cations. Therefore, the FDI architecture can be utilized with electroactive materials exhibiting high selectivity factors for Na^+ to enable energy efficient separations for such applications.

4.2: Sodium superionic conductors (NASICON) in electrochemical separations

NASICONs (Sodium Superionic Conductors) have been widely studied in the context of solid-state electrolytes and cathodes for non-aqueous and aqueous batteries.^{104–115}

Given the high charge capacity and fast solid state ionic diffusion displayed by NASICONs, particularly for Na^+ ions, they make attractive candidates for investigating selective removal of Na^+ in faradaic deionization along with desalination of sea/brackish water resources. Among this class of materials, sodium vanadium phosphate, i.e., $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ (NVP) is a promising material for use in FDI applications. NVP shows high specific capacity ($\sim 118 \text{ mAh/g}$) and has a density almost twice that of typical PBAs (3.25 g/cm^3 vs 1.8 g/cm^3 for PBAs),^{116–119} leading to almost thrice the volumetric charge storage capacity of PBAs. Such a large volumetric capacity is desirable for achieving high water recovery and desalination of concentrated brines ($>0.5\text{M}$ salt). Further, the standard reduction potential $\text{V}^{3+/4+}$ couple for the intercalation of Na^+ in NVP is $\sim +0.3 \text{ V}$ vs Ag/AgCl , which is highly suitable for applications in aqueous electrolytes^{120,121} Moreover, high temperature heating process ($>700^\circ\text{C}$) typically required to obtain NASICONs facilitates incorporation of organic precursors like glucose and citric acid in the reagents, which undergo carbothermal reduction during the heating step to give carbon coated particles.^{105,122} The carbon coating can greatly enhance electronic conductivity of the porous electrode, which can improve rate capability of the material, as discussed in chapter 1. Therefore, carbon coated NVP (NVP/C) and its vanadium-based derivatives are explored for application in FDI in this work.

4.2.1 Synthesis and characterization of sodium vanadium phosphate (NVP) using ball milling and sol-gel techniques

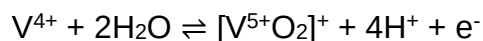
A high-speed ball milling process was adopted from literature¹²². Briefly, sodium metavanadate (NH_4VO_3 , Sigma-Aldrich) and sodium dihydrogen phosphate ($\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$) were weighed in 3:2 molar ratio, with 2 g of NH_4VO_3 and 3.54 g of $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$. Glucose powder with 15% of the total weight of these reagents was added to this mixture in a 20 mL zirconia bowl with ZrO_2 balls (1 mm diameter). A ball to powder weight ratio of 5:1 was employed, and 1-Butanol was chosen as the dispersant for wet milling, due to its high boiling point (118°C). The mixture was milled in a Fritsch planetary ball mill (Pulverisette 7) at 850 rpm for 12 to 18 hours, with 5-minute milling and 5-minute resting period for each cycle. The greenish yellow powders obtained were transferred to porcelain containers, and heated in a quartz tube furnace under Ar or N_2 flow of 2 L/min. A ramp rate of 3°C/minute was used to heat the powders at 350°C for 5 hours, followed by heating at 800°C for 12 hours. Based on electrochemical cycling results discussed in the next section, several other attempts were made using precursors such as V_2O_5 , V_2O_3 as vanadium sources instead of NH_4VO_3 , and dextrose, sucrose as carbon sources instead of glucose.

Along with ball milling, sol-gel process was also attempted to synthesize NVP/C, to compare and optimize the synthesis routes. Briefly, NH_4VO_3 and citric acid were mixed in DI water in 1:1 ratio at ~ 80°C, under vigorous stirring. Citric acid acts as a reducing as well as a chelating agent. The solution was stirred until the color changed from orangish yellow to dark blue, indicating complete reduction of V^{5+} to V^{4+} in the solution. The solution was heated for few hours at 80°C, until a thick bluish green xerogel remained. This gel was transferred to porcelain containers and heated in an inert atmosphere, with the same

heating parameters as described above for the ball milled powders. X-Ray diffraction (Bruker, D8) was used to confirm the crystal structure, which agreed well with literature. Porous electrodes with Ketjen black conducting additive and PVDF binder were fabricated as described in section 2.2.1.

4.2.2 Electrochemical cycling performance of NVP

The porous electrodes of NVP/C obtained from both synthesis routes described above were tested under galvanostatic conditions in a flooded cell setup, with 500 mM NaCl, Ag/AgCl reference and graphite rod counter electrode. Fig 4.1(a) shows a potential vs specific capacity profile obtained during galvanostatic cycling with these electrodes, indicating complete loss of capacity post the first charging cycle. Fig. 4.1 (b) shows a picture of the flooded cell setup, with the yellow color of the electrolyte obtained after the first charging cycle. With any synthetic iteration of NVP/C that was attempted, such as a different vanadium source, change in nature and concentration of organic precursors, and change in the final heating temperature (varying between 800°C and 900°C), the same rapid capacity fade trend and yellowing of the electrolyte was observed. These experiments clearly indicate that NVP/C is not stable for operation in aqueous electrolytes. The yellow discoloration is strongly suggestive of the V^{5+} species. Upon further investigation, it was found that V^{4+} is highly soluble in aqueous electrolytes, according to the following possible reaction scheme ¹²³ :



Therefore, in aqueous electrolytes, the $V^{4+/5+}$ redox couple cannot be utilized to (de)intercalate Na^+ ions, as is routinely done in non-aqueous electrolytes.

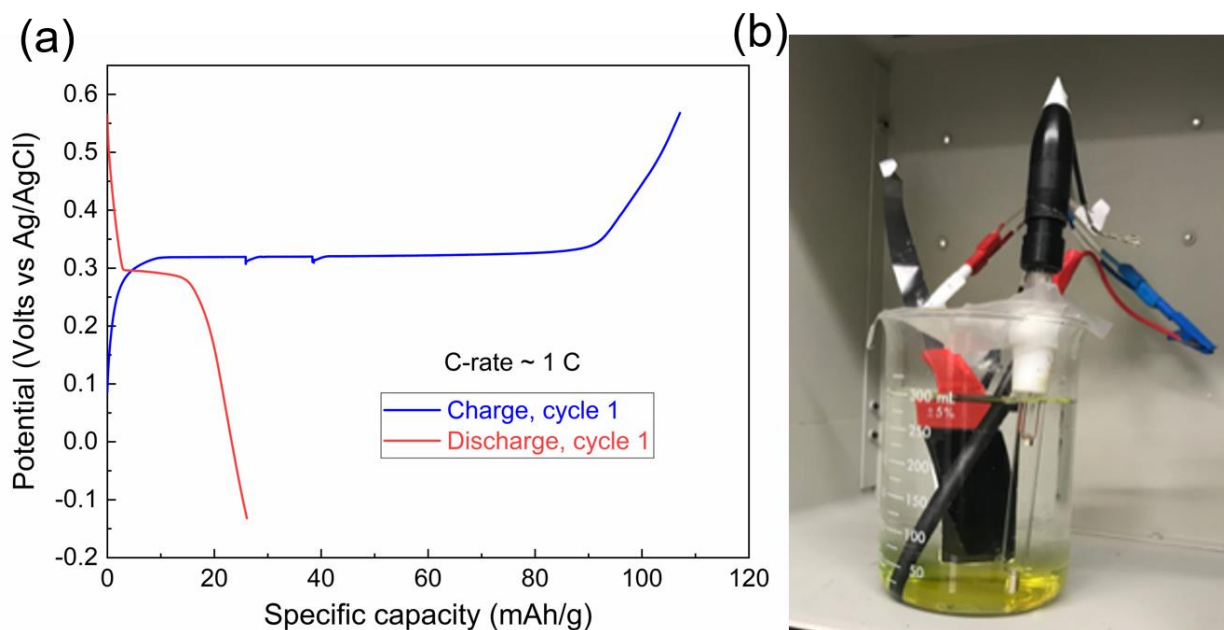


Figure 4.1: (a) Potential vs specific capacity in first cycle obtained during galvanostatic cycling of NVP/C in 500 mM NaCl, and (b) flooded cell setup post 1st charge cycle, with yellowish color of electrolyte indicating vanadium dissolution.

Several authors try to circumvent this issue by modifying the electrolyte. Using ‘water-in-salt’ electrolytes with a very high concentration of supporting salts alters the equilibrium for vanadium dissolution, leading to a more stable cycling performance, although degradation is not completely stopped.¹²⁴ However, while electrolyte modification can work in energy storage applications, the scope of such an approach is limited in context of FDI. The electrolyte in an FDI cell is largely determined by the incoming feed stream depending on the source and the target application, which can rarely be modified, if at all. Further, dissolution of metals such as vanadium can cause a major safety hazard when considering an electrochemical separation operation. Therefore, alternate strategies are needed to stabilize this material for long term cycling.

4.2.3: Stabilization of NVP/C in aqueous electrolytes using titanium alloying

To prevent active dissolution of vanadium in NVP during oxidation, one route can be to dope or alloy this material with Titanium (Ti) based derivatives. Sodium titanium phosphate ($\text{Na}_3\text{Ti}_2(\text{PO}_4)_3$ or NTP) is another material in the NASICON family, which reversibly intercalates sodium.^{125,126} This material has been extensively explored for use as the anode in aqueous and non-aqueous batteries, due to its low reduction potential for Na^+ intercalation (-0.8 V vs SHE) and relatively stable cycling performance.^{127–129} Unlike vanadium oxides, titanium oxides are highly insoluble in aqueous electrolytes. While NTP itself is not favorable for aqueous FDI due to its extremely low reduction potential, surface coating of NVP with a thin layer of titanium-based compound such as NTP or TiO_2 can likely prevent dissolution of the vanadium, since only titanium ions in the crystal will be majorly exposed to the water molecules.

Therefore, coating of NVP/C with NTP and TiO_2 was attempted. The sol-gel process was used to synthesize NVP/C particles, and three variants to the step of adding titanium-based precursors were tested, labelled as NVP-Ti-(i), NVP-Ti-(ii) and NVP-Ti-(iii). Briefly, titanium isopropoxide ($\text{Ti}(\text{OCH}_2\text{CH}_2)_4$, abbreviated as $\text{Ti}(\text{OR})_4$) dissolved in ethanol was used as the titanium source in the sol-gel process, and the variants were synthesized as follows:

NVP-Ti-(i): NVP/C particles were made using the same process as described in section 4.2.1. The NVP/C particles were hand grinded and dispersed in an aqueous solution with dissolved NaH_2PO_4 under vigorous stirring. Titanium isopropoxide in ethanol was added to the above mixture at room temperature, such that mole fraction of Ti was 15% of V in NVP/C. This mixture was heated at 80°C to evaporate the water and ethanol, to obtain

black NVP/C powders coated with a whitish 'gel' corresponding to Ti(OR)_4 and NaH_2PO_4 . These powders were heated in a tube furnace at 800°C for 10 hours, to obtain NVP/C/NTP/C. note that the interface between NVP and NTP might be complex, and an alloy may have formed at the interface instead of separate phases of NVP and NTP.

NVP-Ti-(ii): In this process, an attempt to 'double coat' NVP/C with NTP/C was made. Sol-gel process for making NVP was followed, but the NTP/C was added in two different steps. First, after obtaining the xerogel of NVP as described in section 4.2.1, the powders were heated in inert atmosphere at 350°C for 5 hours. The brownish powders so obtained were coated with precursor for 10% molar ratio of NTP/C with the same process as described above for NVP-Ti-(i). These powders were further heated at 800°C for 12 hours to complete the formation of the crystalline phases of NVP and NTP. Second, the black powders obtained after heating (presumably NVP/C/NTP/C) were again dispersed to form sol-gel in 10% NTP/C precursor solution, and reheated at 800°C to add an additional layer of NTP/C.

NVP-Ti-(iii): Ti(OR)_4 is a very well-studied precursor for making TiO_2 nanoparticles.¹³⁰ Therefore, NVP/C particles obtained after sol-gel process were ball milled in a zirconia bowl with Ti(OR)_4 in butanol for 2 hours, at 800 rpm with 5:1 weight ratio of zirconia balls to NVP/C powder.

Fig. 4.2 shows the galvanostatic cycling performance of NVP-Ti-(i)/(ii)/(iii) in 500 mM NaCl, compared to pure NVP/C. While NVP loses all its capacity post oxidation in the 1st charge cycle as discussed previously, alloying/coating with Ti based compounds slows down the capacity degradation considerably. Note that the overall specific capacity will be lower for Ti doped NVP because Ti is not electroactive in the potential range of interest.

However, while we see definite improvement in performance by coating/forming alloys with Ti-based compounds, the capacity fade is still quite severe. Vanadium still readily dissolves during oxidation and renders a yellowish color to the electrolyte as seen earlier with pure NVP/C.

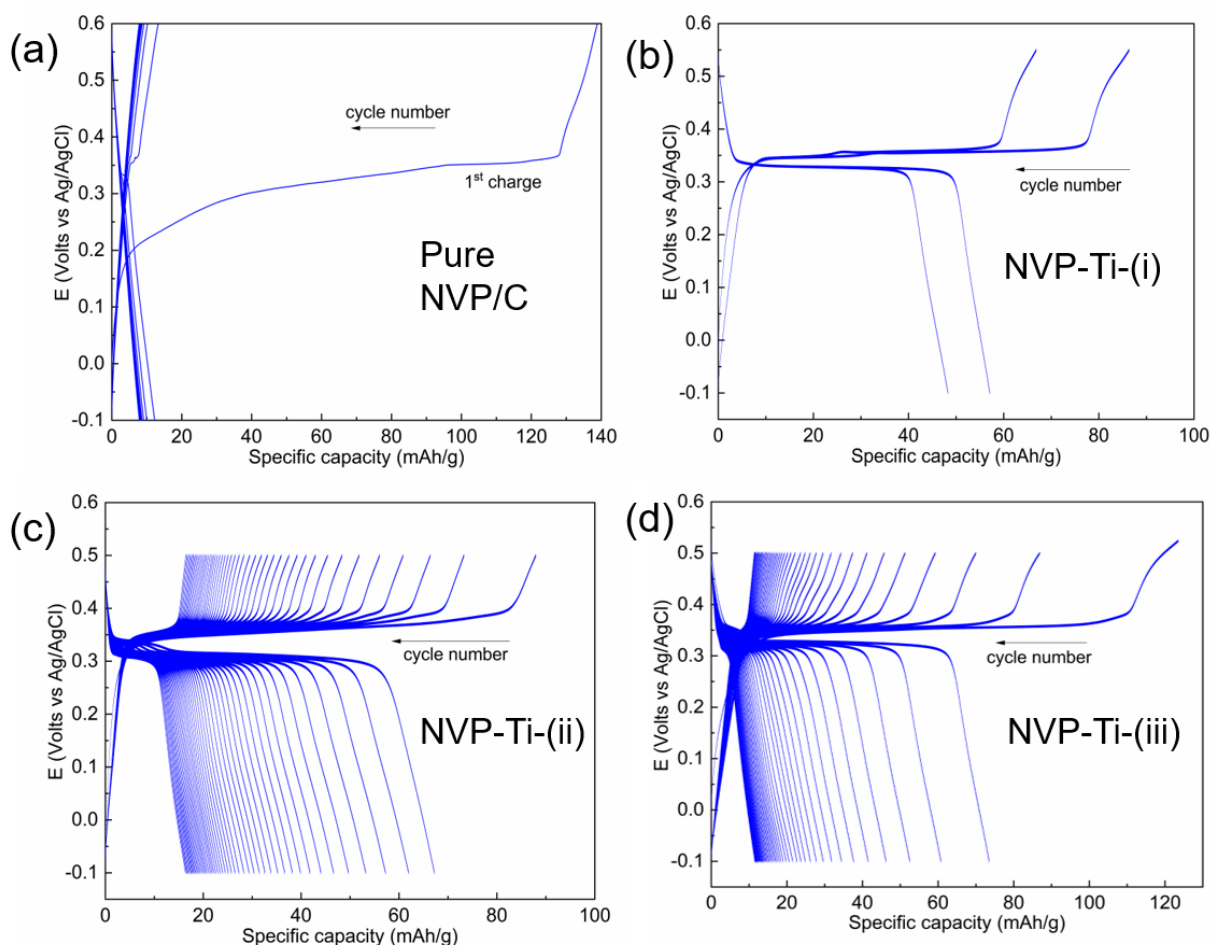


Figure 4.2: Galvanostatic cycling performance in 500 mM NaCl for (a) pure NVP/C, (b) NVP-Ti-(i), (c) NVP-Ti-(ii), and (d) NVP-Ti-(iii). Coating/alloying NVP/C with 10% Ti-based compounds considerably slows down capacity fade.

Therefore, increasing the mole fraction of titanium in the alloys can stabilize NVP further. Fig 4.3 shows galvanostatic cycling performance NTVP, i.e., alloy formed by 50% doping of Ti, to form $\text{Na}_2\text{TiV}(\text{PO}_4)_3$ (confirmed through X-ray diffraction and X-ray fluorescence). The capacity stabilizes after 10 cycles, with overall capacity fade $\sim 2.2\%$ and the

coulombic efficiency reaching >99.5%. Similar results have recently been shown in literature to make symmetric Na-ion batteries in aqueous and non-aqueous electrolytes,^{120,123,125,131} although in electrolytes with higher salt concentration.

However, since titanium is not electroactive in the potential range of interest, increasing the percentage of Ti in the overall composition will decrease the specific capacity. Therefore, 50% Ti incorporation will lead to half the specific capacity of NVP/C (i.e., ~50-60 mAh/g for NTVP vs 118 mAh/g for NVP). Even though the specific capacity is decreased, the volumetric capacity of NTVP ($\text{Na}_2\text{TiV}(\text{PO}_4)_3$) can still be expected to be close to or higher than PBAs, due to the high mass density of NTVP ($\sim 3 \text{ g/cm}^3$).

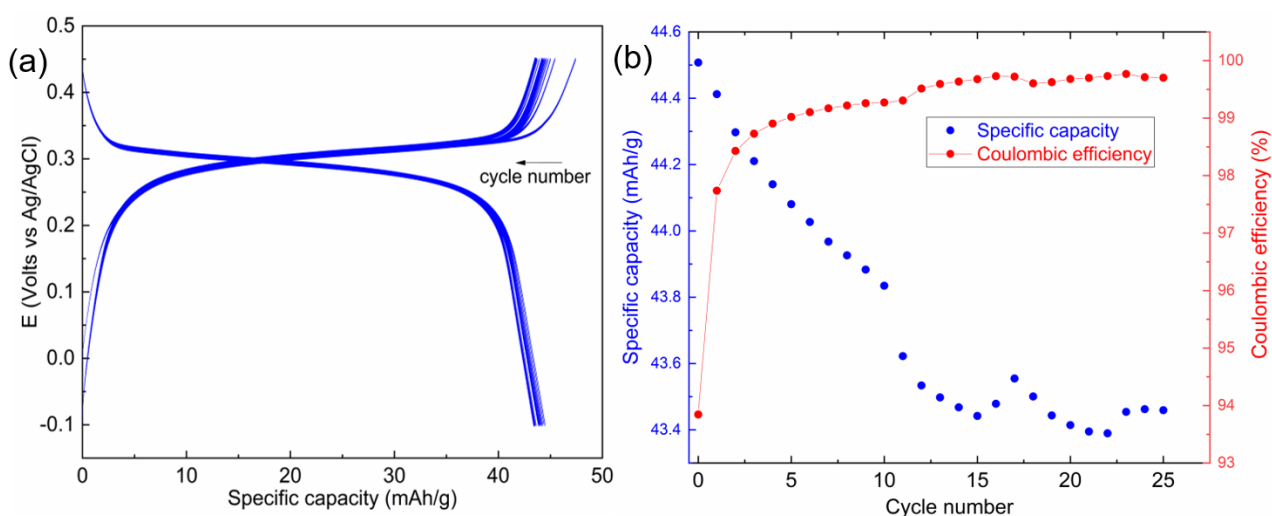


Figure 4.3: Galvanostatic cycling performance of $\text{Na}_2\text{TiV}(\text{PO}_4)_3$ in 500 mM NaCl, with (a) potential vs specific capacity at 1C, and (b) variation of specific capacity and coulombic efficiency with cycle number.

While the synthesis of NTVP has been discussed briefly, the multistep process involving sol-gel formation followed by two stage heating of the powders renders itself to significantly higher complexity than coprecipitation based synthesis of PBAs. There are many parameters to optimize in the synthesis process. The sol-gel step requires careful selection of reagents and synthesis conditions. The stability and electrochemical

performance of the final product depends on many factors both in the sol-gel formation and drying step, as well as heating the resulting xerogel in a tube furnace. In terms of reagents, the choice of vanadium and titanium precursors, nature, and concentration of organic precursors for reduction and chelation of aqueous vanadium and titanium, pH of the reaction, solvents and relative amounts used for dissolving vanadium and titanium sources are all crucial to obtain the final product, to repeatably obtain specific capacity between 40 to 45 mAh/g, and a low rate of capacity fade. Further, the final performance of the product is also dependent on the two-stage heating process, wherein the size and shape of containers, temperature ramp rate, inert gas flow rate, and temperature during heating at both moderate (around 350°C) and high temperature steps (around 800°C) are crucial in obtaining the final product with minimal capacity losses.

Two key steps were found to be most impactful, which are not generally discussed in literature: (i) stabilization of titanium isopropoxide precursor, by using ethanol solvent with dissolved citric acid or glacial acetic acid and cooling down the aqueous vanadium precursor solution at room temperature before mixing the two solutions. These measures avoid formation of ill-defined titanium oxo-hydroxo precipitates during mixing; and (ii) maintaining an inert gas flow rate of close to 2-3 L/min during heating, to ensure no contamination by oxygen gas occurs. Failure to adhere to either of these steps gave lower specific capacity (around 35 mAh/g) and faster degradation with poor repeatability of results.

4.3: Understanding atomic arrangements in $\text{Na}_2\text{TiV}(\text{PO}_4)_3$ crystal lattice

X-ray diffraction resolved the crystal structure of NTVP in the $R\text{-}3c$ space group, with $a=8.6 \text{ \AA}$ and $c=21.8 \text{ \AA}$, in good agreement with literature.¹¹² First principles electronic structure calculations were performed to investigate whether there are preferred atomic configurations within NTVP crystal and understand how its structure might be different from NVP or NTP. Experimentally, it is difficult to resolve the exact relative positions of Ti and V atoms in the bulk of the NTVP crystal lattice, due to their similar atomic masses. Fig. 4.4 shows various possible arrangements of Ti and V in the crystal, for $\text{Na}_1\text{TiV}(\text{PO}_4)_3$.

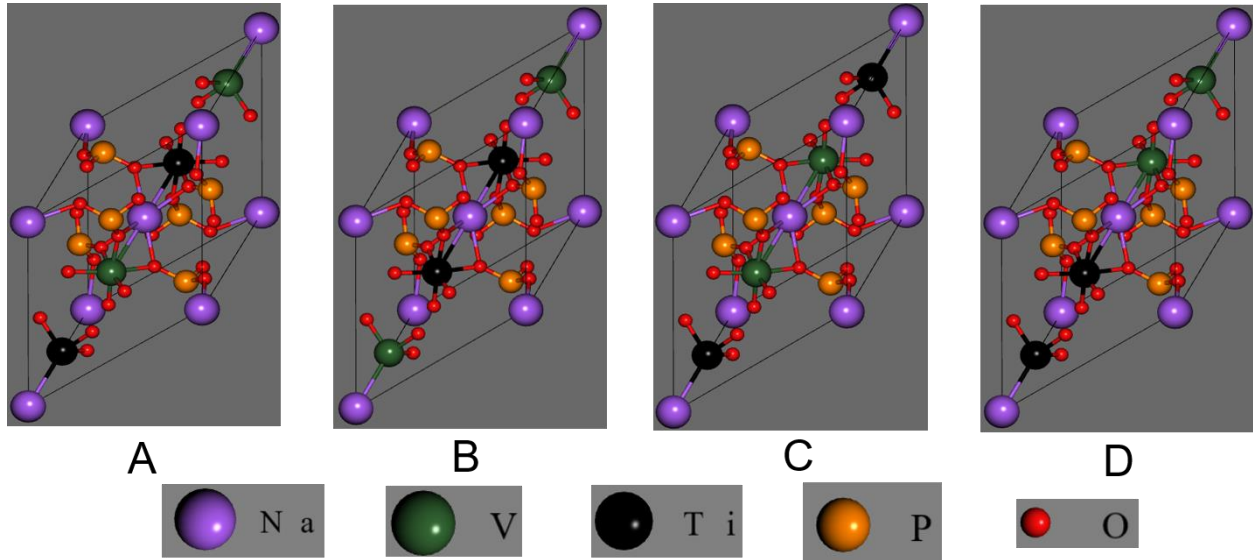


Figure 4.4: Configurations for $\text{Na}_1\text{TiV}(\text{PO}_4)_3$ with different arrangements for Ti and V atoms in the crystal.

Density functional theory (DFT) calculations were performed with collinear spin-polarization using the Quantum ESPRESSO (QE) package.⁸⁸ Correlation interactions were modelled using the generalized gradient approximation with the Perdew–Burke–Ernzerhof (PBE) functional and Hubbard corrections (GGA +U).^{89–91} The U values for Ti and V were taken to be 4.2 eV and 4 eV respectively.¹³² The valence electrons for Ti, V, and Na atoms corresponded to $3d^24s^2$, $3d^34s^2$, and $2s^22p^63s^13p^0$,

whereas the remaining electrons were kept frozen as core states. Scalar-relativistic projector augmented wave pseudopotential (PAW) were employed to describe the interaction between valence and frozen electrons. A cutoff energy of 1088 eV was used in all cases for the truncation of plane-wave basis sets. Monkhorst–Pack k -points were used in every calculation with a $3 \times 3 \times 3$ grid for the $2 \times 2 \times 1$ supercell. Charge density was smeared in each relaxation calculation using gaussian smearing scheme. Internal relaxation calculations were performed by relaxing atomic coordinates while fixing supercell symmetry as R-3c, in accordance with experimental X-ray diffraction data.¹¹² The lattice constant for each configuration was varied until a final pressure less than 0.1 kbar was obtained, while retaining the rhombohedral symmetry of the supercell. Fig. 4.5 shows the top view for NTVP in config. A with various degrees of intercalation of Na^+ .

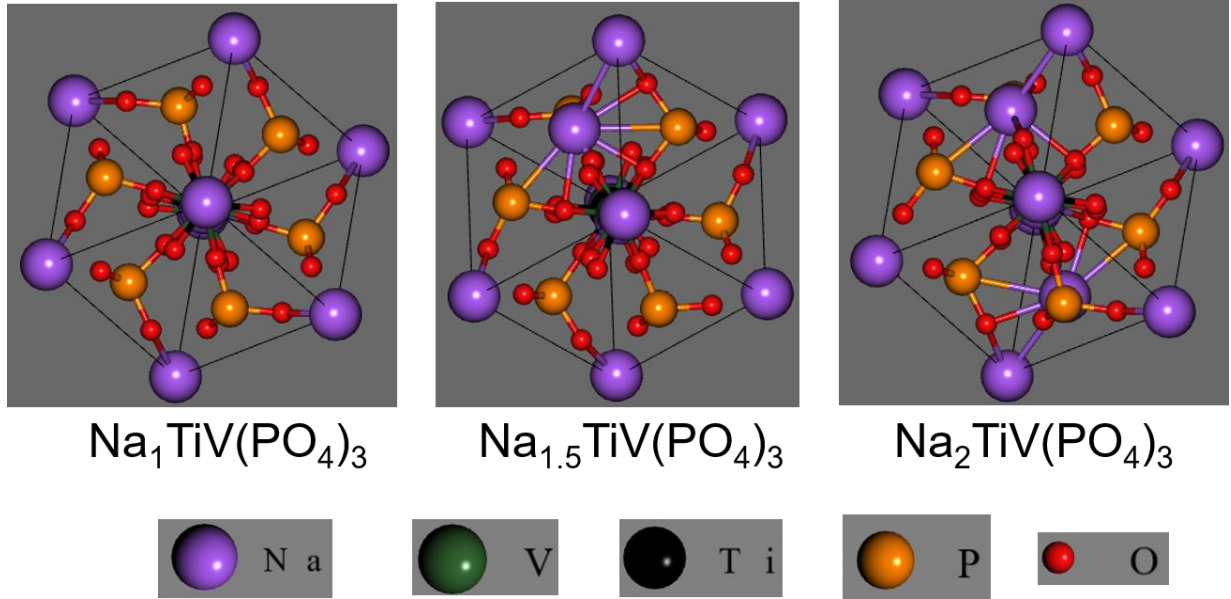


Figure 4.5: Top view for NTVP (config A, Fig. 4.4) with different degrees of intercalation of Na^+ .

For each degree of intercalation, Na^+ ions were assigned positions within the interstitial sites, and a set of configurations was obtained by exhaustively permuting the occupations of Ti and V ions. For fixed interstitial position(s) of Na^+ ion(s) at each degree of

intercalation, there are 6 total configurations (i.e., $4!/(2!2!)$) corresponding to Ti and V rearrangements. Fig. 4.6 shows all configurations for $\text{Na}_{1.5}\text{TiV}(\text{PO}_4)_3$, which has the least symmetry. Relative energies in terms of kT (where k is the Boltzmann constant and temperature, $T=298\text{K}$) are compared to the least energy structure (A2) and labelled for each configuration (i.e., $E_{i,\text{relative}} = E_i - E_{A2}$, where E_i is the energy of the i^{th} configuration).

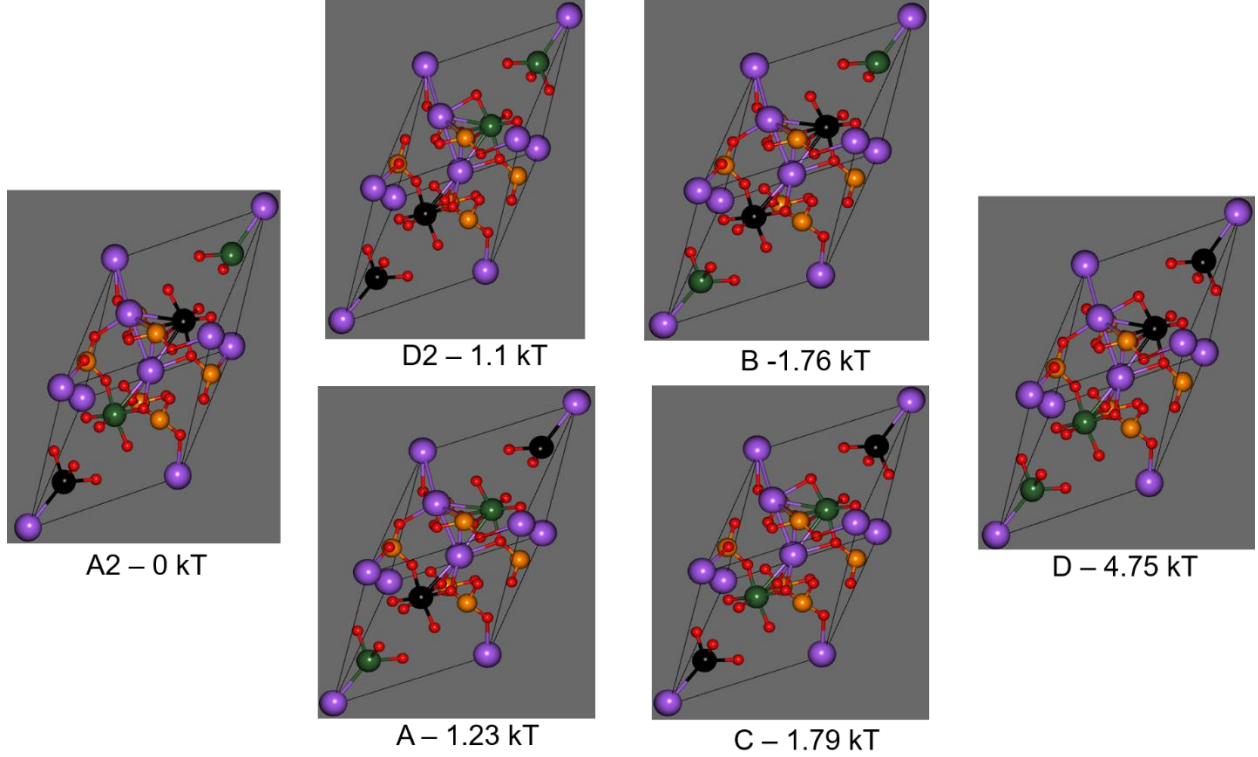


Figure 4.6: Configurations obtained for $\text{Na}_{1.5}\text{TiV}(\text{PO}_4)_3$ by rearranging Ti and V ions in a $2\times 1\times 1$ supercell, labelled with relative energy compared to minimum energy configuration (A2).

For $\text{Na}_1\text{TiV}(\text{PO}_4)_3$ and $\text{Na}_2\text{TiV}(\text{PO}_4)_3$, configurations A2 and D2 are degenerate with A and D because of symmetry. For a fixed degree of intercalation, the volumes of all configurations were found to be within 0.08% of each other.

Probability of each configuration was calculated using an NPT ensemble analysis. At a pressure (P) of 1 atm and a maximum volume (V) of $486 \text{ \AA}^3$ (corresponding to $\text{Na}_2\text{TiV}(\text{PO}_4)_3$ for these supercells, $PV \sim 0.01 kT$, which is more than an order of

magnitude smaller than relative energies of non-degenerate configurations at any degree of intercalation. Therefore, an NPT ensemble analysis was performed to compare relative probability of each configuration while neglecting the PV term. For a configuration with energy E_i , the probability $p(E_i)$ is given as:

$$p(E_i) = \frac{\omega_i \exp\left(-\frac{E_i}{kT}\right)}{\sum_i \omega_i \exp\left(-\frac{E_i}{kT}\right)}, \text{ where } \omega_i - \text{ degeneracy for } i^{\text{th}} \text{ configuration} \quad (4.1)$$

These results are summarized in table 4.1 below.

Configuration	NaTiV (PO ₄) ₃	Na _{1.5} TiV(PO ₄) ₃	Na ₂ TiV(PO ₄) ₃
A	0.131	0.148	0.005
B	0.343	0.087	0.331
C	0.333	0.085	0.345
D	0.193	0.004	0.319
D2		0.169	-
A2	-	0.507	-

Table 4.1: Probabilities based on NPT ensemble analysis for each configuration corresponding to different Ti, V arrangements in the NTVP lattice.

As evidenced from table 4.1, there is no single configuration which is significantly more preferred compared to the others, especially at the terminal degrees of intercalation. Recall that the NTVP particles are synthesized in the fully intercalated state (Na₂TiV(PO₄)₃). Therefore, Ti and V will most likely be disordered at the transition metal sites in the NTVP crystal structure post synthesis. This disorder of transition metals contrasts with PBAs like NiHCF_e, where positions of nickel and iron are fixed based on

preferred coordination with nitrogen and carbon, respectively. Further, for $\text{Na}_{1.5}\text{TiV}(\text{PO}_4)_3$, the much higher preference for configuration A2 over D (despite the Na atom being coordinated to Ti in both cases) suggests that there are complex interactions between Ti-Ti, V-V and Ti-V within NTVP which determine the energy and structure of the crystal. Only few early theoretical efforts attempt to understand bonding among such transition metals.^{133,134} Considering how important Ti is to the stability of NTVP particles in aqueous electrolytes, the findings in this section warrant future investigation into deeper understanding of the interactions between Ti, V and Na. This understanding is especially important for resolving the surface structure of NTVP crystal, which will give insights into the mechanisms determining stability of this compound during electrochemical oxidation and inform future synthesis efforts for stabilizing NVP with Ti based compounds to obtain higher charge storage capacity.

4.4: Cation insertion mechanism within NTVP

Since a relatively new derivative in NASICON family was synthesized, it is important to understand the mechanisms of (de)insertion of alkali cations within this material to gain insights into its operation during electrochemical cycling.

NVP and NTP exhibit phase separation during intercalation of Na^+ ions, in non-aqueous and aqueous electrolytes, which is characterized by a flat plateau in plot of electrochemical potential vs specific capacity or degree of intercalation.¹²¹ However, galvanostatic cycling of NTVP at 1C (Fig. 4.3(a)) indicates formation of a solid solution during (de)intercalation of Na^+ ions. The physics of phase separation and solid solution formation using a simple regular solution model is explained in the next section, followed

by a deeper analysis of equilibrium potential curve of NTVP in section 4.4.2 and its implications on Na⁺ intercalation into the crystal.

4.4.1: Physics of phase separation and regular solution model

During a typical intercalation process, solute ions are inserted into interstitial sites in a host crystal. As the degree of intercalation increases, these ions are redistributed within the host lattice, such that the Gibbs free energy of the system is minimized when operating at or close to equilibrium. To quantitatively understand this phenomenon, a relatively simple model describing mixing of different types of atoms can be utilized. Fig. 4.6 shows two extreme scenarios of mixing between two types of atoms 'A' and 'B'. The atoms can either form a homogenous mixture, i.e., a solid solution, or form 'A-rich' and 'B-rich' regions, to form two separate phases. The tendency of a system to form either a solid solution or phase separated mixture depends on the magnitude of energy of interaction(U) between each kind of atom(s), i.e, U_{A-A} , U_{B-B} and U_{A-B} . The difference in the magnitudes of these energies gives rise to an 'interaction parameter (Ω)',¹³⁵ which is related to the energies as:

$$\Omega \propto \frac{1}{2}(U_{A-A} + U_{B-B}) - U_{A-B} \quad (4.2)$$

The corresponding change in internal energy, ΔU^{mix} can be modeled as:

$$\Delta U^{mix} = \Omega x_A x_B, \quad (4.3)$$

where x_i represents the mole fraction of the i^{th} atom in the mixture. Therefore, for favorable mixing, $\Delta U^{mix} \leq 0$, which implies $\Omega \leq 0$, i.e., energy released due to interaction of A and B atoms is higher than the average sum of cohesive energies between A-A and B-B. For positive Ω , phase separation is energetically favored.

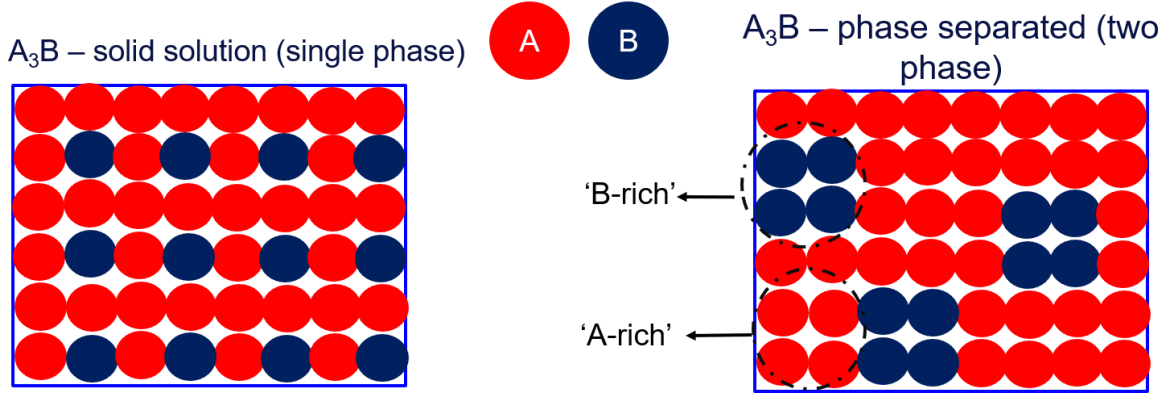


Figure 4.7: Simple model depicting formation of solid solution or phase separated mixture during mixing of two different atoms A and B

Further, due to mixing of these two species, entropy of mixing can be quantified based on the number of microstates that can be formed in the new configuration. Change in entropy of the mixture (ΔS^{mix}) can be estimated based on Boltzmann entropy as:

$$\Delta S^{mix} = k_B \log \left(\frac{(N_A + N_B)!}{(N_A)!(N_B)!} \right) \quad (4.4)$$

Where k_B is the Boltzmann constant, and N_A , N_B are the number of atoms of A and B respectively. By defining mole fractions of each atom, $x_A = N_A/(N_A + N_B)$ and $x_B = N_B/(N_A + N_B)$, where $x_A + x_B = 1$, the expressions for internal energy and entropy can be reformulated in terms of mole fractions. The Gibbs free energy of mixing can be written as:

$$\Delta G^{mix} = \Delta H^{mix} - T\Delta S^{mix} \cong \Delta U^{mix} - T\Delta S^{mix}, \text{ neglecting PV work} \quad (4.5)$$

Further, defining mole fraction of solute molecules, $x_B = x$, implying $x_A = 1 - x$, the above equation can be rewritten as:

$$\Delta G^{mix} = \Omega x(1 - x) - k_B T [x \log(x) + (1 - x) \log(1 - x)] \quad (4.6)$$

Therefore, the electrochemical potential can be derived from the expression of Gibbs free energy, by using $\mu = \left(\frac{\partial G}{\partial n} \right)_{T,P}$ and $\Delta G = -FE$, for a single electron transfer reaction:

$$E = E^0 + \left(\frac{RT}{F}\right) \log\left(\frac{1-x}{x}\right) + \Omega(2x - 1) \quad (4.7)$$

Where E^0 is the standard reduction potential of the reaction.

When Ω is close to 0, the Nernst equation for equilibrium potential is obtained, which is approximately exhibited by PBAs, as depicted in Fig. 2.3 (b). For non-zero interaction parameters, phase separation or homogenous mixing depends on both magnitudes of energies of interaction as well as changes in entropy of the system.

Note that the model assumes that the concentration of solute atom (B) can go from absolute 0 to 100% in the system. However, in PBAs and NASICONs, at least 50% of the sites are always occupied by Na^+ (or other intercalant atoms), to maintain charge neutrality. Therefore, fraction of solute atoms is never completely zero, and hence accuracy of the regular solution model will decrease at low intercalation fractions for real systems.

4.4.2: Understanding Na^+ intercalation in NTVP

To understand the interaction of Na^+ ions with NTVP host lattice, equilibrium potential curves in 500 mM NaCl were obtained through multiple techniques – galvanostatic cycling at slow C-rate (C/6), potentiostatic intermittent titration (PITT) with the same procedure as described in section 2.2.3, and galvanostatic intermittent titration (GITT). In GITT experiments, small constant current pulses (C/40) were applied for 5 mins, injecting 2.5% of the total charge capacity at each GITT step. Each current step was followed by relaxation for 40 mins. All equilibrium potential curves obtained from these experiments agreed to within 5% of each other.

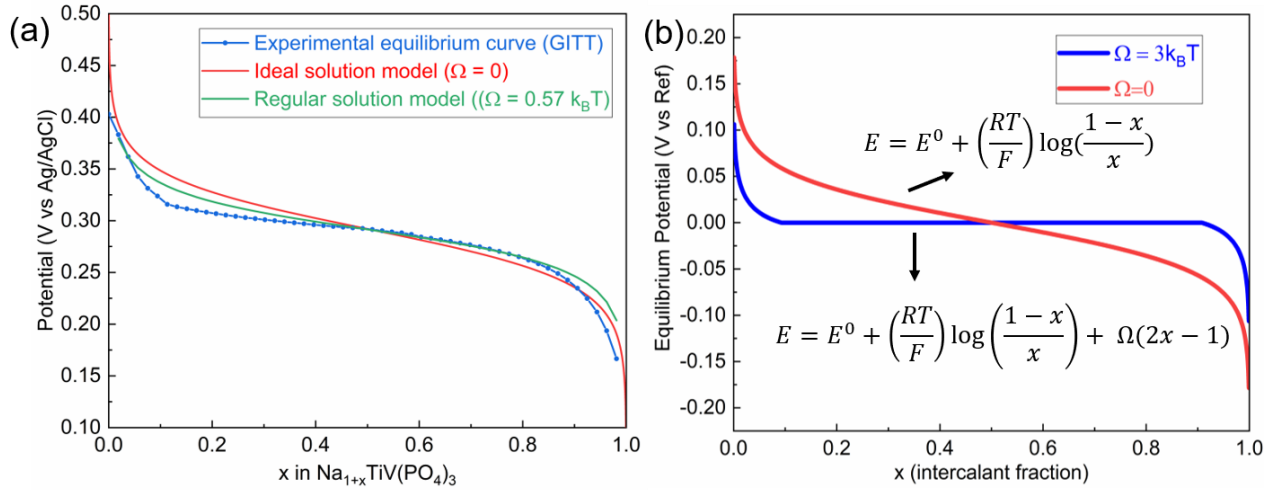


Figure 4.8: (a) Experimentally obtained equilibrium potential curve from GITT, compared to fitted curve using regular solution model, and (b) simulated equilibrium potential curves for a regular solution model by varying the interaction parameters for a hypothetical system, with $E^0 = 0\text{V}$.

Fig. 4.7(a) shows the equilibrium potential curves obtained after GITT, and fitted to a regular solution model, to obtain an interaction parameter of $0.57k_B T$. An ideal solution model, i.e., with $\Omega=0$ is shown for comparison. Fig. 4.7(b) shows simulated equilibrium potential curves, examining the effect of changes Ω . The flat potential plateau at a high interaction parameter value of $3k_B T$ indicates phase separation into two distinct phases, as observed in NTP and NVP. Based on the Gibbs phase rule relating degrees of freedom (F) to the total number of chemically different constituents (C) and phases (P) in the system (i.e., $F=C-P+2$), electrochemical potential must remain constant for a two-phase system due to interaction of two distinct chemical species (intercalating ion and host lattice in this case) when the experiment is performed at a constant temperature and pressure. Therefore, alloying of NVP with titanium reduces the interaction parameter of the Na^+ ions with the host lattice, avoiding phase separation. However, the interaction of Na^+ ions being (de)intercalated with the NTVP crystal is significantly higher than a PBA, leading to a non-nernstian dependence of equilibrium potential on intercalant fraction.

4.5: Selectivity of Na⁺ intercalation in NTVP

As alluded to earlier in section 4.1, considering the affinity for intercalation Na⁺ of ions in NASICON materials, it is prudent to investigate how different alkali and alkaline earth ions insert into these materials. Fig 4.8 shows galvanostatic cycling data for NTVP electrodes separately cycled in aqueous electrolytes with 500 mM of Li⁺, Na⁺, K⁺, Mg²⁺ and Ca²⁺. Several notable trends can be observed. Firstly, as discussed earlier, Na⁺ shows stable cycling with specific capacity between 40 to 45 mAh/g. Li⁺ also shows stable cycling with a solid solution intercalation profile, and a specific capacity of approx. 30 mAh/g which is 33% lower than the capacity for Na⁺. Further, standard reduction potential of Li⁺ is ~ 70 mV lower than that of Na⁺ (0.24 V for Li⁺ vs 0.31 V for Na⁺, vs Ag/AgCl). This difference in reduction potentials implies a selectivity ratio of approximately 16:1 for Na⁺ to Li⁺, at equilibrium (calculated as $\exp(-\Delta E^0 / k_B T)$, where $\Delta E = 70$ mV, and $k_B T = 25$ mV at room temperature). The ~33% lower capacity for Li⁺ insertion compared to Na⁺ indicates there are likely 1/3rd of the sites in the NTVP crystal that are not accessible for storage of Li⁺ ions, where only Na⁺ can insert. Secondly, all alkali/alkaline earth cations apart from Li⁺ and Na⁺ show a purely capacitive response and hence a very low specific capacity (5-6 mAh/g), indicating there is no intercalation of these ions into the NTVP crystal structure. Therefore, these results indicate a selectivity sequence of Na⁺(aq) >> Li⁺(aq) >>> K⁺(aq), Mg²⁺(aq), Ca²⁺(aq) for intercalation in NTVP.

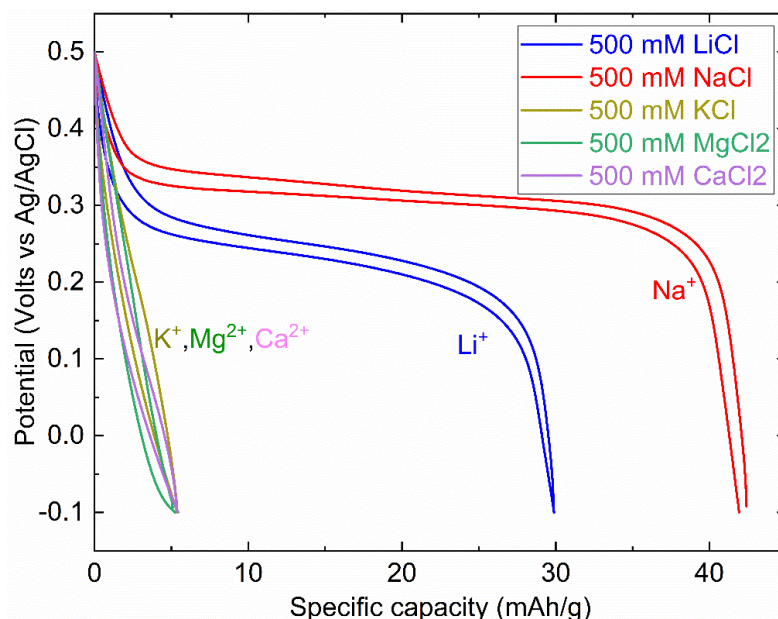


Figure 4.9: Comparison of galvanostatic cycling performance of NTVP in aqueous electrolytes with alkali and alkaline earth cations (500 mM LiCl, NaCl, MgCl₂, and CaCl₂).

Table 4.2 lists the bare ionic radii, hydrated radii, and atomic weights of the cations.¹³⁶

Unlike PBAs, where selectivity increases with increasing molecular weight or decreasing hydrated ionic radius ($\text{Cs}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$),^{3,137} no clear trend is shown by NTVP. As evidenced from table 4.1, there seems to be a hard threshold for ions with the product of nominal charge and atomic weight greater than 11. This trend suggests that the energetics of intercalation in NTVP are such that the interstitial sites are highly suited for insertion of Na^+ over any other cation.

Cation	Bare ionic radius (pm)	Hydrated ionic radius (pm)	Atomic weight(g/mol)	Nominal Charge (q) X Atomic weight	Intercalation seen?
Li^+	94	382	3	3	Partial
Na^+	117	358	11	11	Yes
K^+	149	331	19	19	No
Mg^{2+}	72	428	12	24	No
Ca^{2+}	100	412	20	40	No

Table 4.2: Radii and atomic weights of alkali/alkaline earth cations tested for intercalation in NTVP

The ultra-high selectivity exhibited by NTVP for Na^+ over other cations can prove beneficial for use in agriculture in saline regions to avoid micronutrient poisoning of plants, as well as preventing sodium contamination of salts during chemical manufacturing (discussed in section 4.2). Therefore, porous electrodes of NTVP were tested in mixed ion solutions to quantify the selectivity of Na^+ over other cations.

Fig. 4.9 shows flooded cell galvanostatic cycling in electrolytes with 100 mM KCl + 100 mM NaCl, and 100 mM KCl + 10 mM NaCl, at a C-rate of 1C and C/2. The variation of potential with capacity clearly indicates solid solution intercalation reaction, which can be mainly attributed to the insertion of Na^+ (aq) ions. The 1C cycling in 100 mM KCl + 10 mM NaCl shows < 50% capacity than with 100 mM KCl + 100 mM NaCl. Further, in the case with only 10 mM NaCl, the discharge and charge curves are highly asymmetric. These results can be attributed to 10:1 ratio of K^+ : Na^+ in the electrolyte. During discharge in the electrolyte with low Na^+ concentration (10 mM), the potential response is limited by the diffusion of Na^+ ions in the electrolyte. Therefore, a semi-linear potential profile is obtained. However, during charging, since Na^+ ions are traveling from within the crystal into the solution, the potential response as a function of intercalant fraction follows the usual solid solution profile. When the applied current is lowered to C/5, solid state diffusion of Na^+ ions within the NTVP porous electrode becomes rate limiting during both discharge and charge, as evidenced by the potential response.

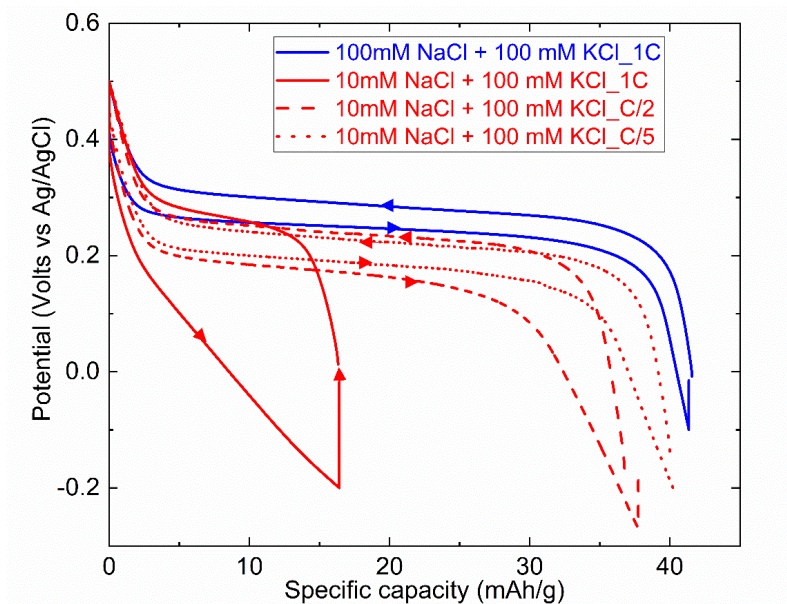


Figure 4.10: Galvanostatic cycling of NTVP in mixed solutions of 100 mM KCl and 100 mM NaCl, 10 mM KCl and 10 mM NaCl at different C-rates.

Based on the specific capacity results obtained by cycling in divalent and trivalent electrolytes, as discussed for Figs. 4.8 and 4.9, a lower bound for the selectivity factor can be calculated for selectivity of Na^+ over K^+ and other ions. For the case of 100 mM KCl + 10 mM NaCl, almost all the capacity at C/5 rate can be attributed to intercalation of Na^+ . From Fig. 4.8, a maximum of 6 mAh/g of K^+ can be absorbed, which can be subtracted from the total specific capacity calculated in the mixed ion solution to obtain the minimum amount of Na^+ intercalated. Note that 6 mAh/g represents purely capacitive adsorption of K^+ , due to the electric double layer(s) at the surface of active material, conducting additive and current collector. In principle, there is no K^+ being inserted into the interstitial sites of NTVP, so technically the selectivity of Na^+ over K^+ is infinite in the material. However, in practical application, there will always be some adsorption of K^+ , and hence a finite selectivity ratio will be achieved. The capacitive response also provides a way of tuning the selectivity ratio of Na^+ and K^+ by modifying the overall surface area of

the particles to some extent. Ball milling of as synthesized NTVP/C particles can be used to increase the surface area and adsorb more K^+ . Presently, for the experiments discussed in Figs. 4.8 and 4.9, selectivity ratio($\beta_{Na/K}$) can be calculated as:

$$\beta_{Na/K} = \frac{\frac{[Na^+ \text{ captured}]}{[K^+ \text{ captured}]}}{\frac{[Na^+ \text{ electrolyte}]}{[K^+ \text{ electrolyte}]}} = \frac{\frac{(40-6)mAh/g}{6 mAh/g}}{\frac{10 mM}{100 mM}} = 56.67$$

Therefore, porous electrodes of NTVP/C are at least 56 times more selective to capturing Na^+ over K^+ . Similar estimates are obtained for Mg^{2+} and Ca^{2+} based on the above calculation. These selectivity ratios are the highest reported so far for bulk selective electrochemical capture of alkali/alkaline earth cations - at least two times as much as observed for Na^+ over Mg^{2+} and Ca^{2+} , and >560 times for Na^+ over K^+ compared to PBAs.¹⁰² Given the promising performance of NTVP for selectivity, the electrodes were assembled in a custom built recirculating FDI cell developed at the Smith lab.

4.6: Operating NTVP electrodes in faradaic deionization cell

The custom built FDI cell at the Smith lab was recently used to demonstrate desalination of brackish water with 100 mM NaCl using PBA electrodes at the Smith lab. The cell accommodates symmetric electrodes around 150 μ m thick with areal dimensions of 1.7 X 1.5 cm², employing a flow through configuration of the target solution to be desalinated. An Arduino controller is used to automatically switch the flow of desalinated and concentrated streams based on completion of the (dis)charge cycle.

NTVP electrodes were fabricated for use in this device and tested with 100 mM NaCl, and 100 mM KCl+10 mM NaCl for selective capture of Na^+ over K^+ . To prepare electrodes for operation in the symmetric configuration, one electrode was completely charged and other was kept as synthesized, in the completely discharged state. Initial condition of

charging both electrodes to 50% SOC was also tested. Fig. 4.11 shows the galvanostatic cycling performance of NTVP electrodes in this FDI cell with 100 mM NaCl, at current density of $1\text{mA}/\text{cm}^2$ ($\sim 3\text{C}$ rate) and flow rate of $1\text{ mL}/\text{min}$, with 5 mL of reservoir.

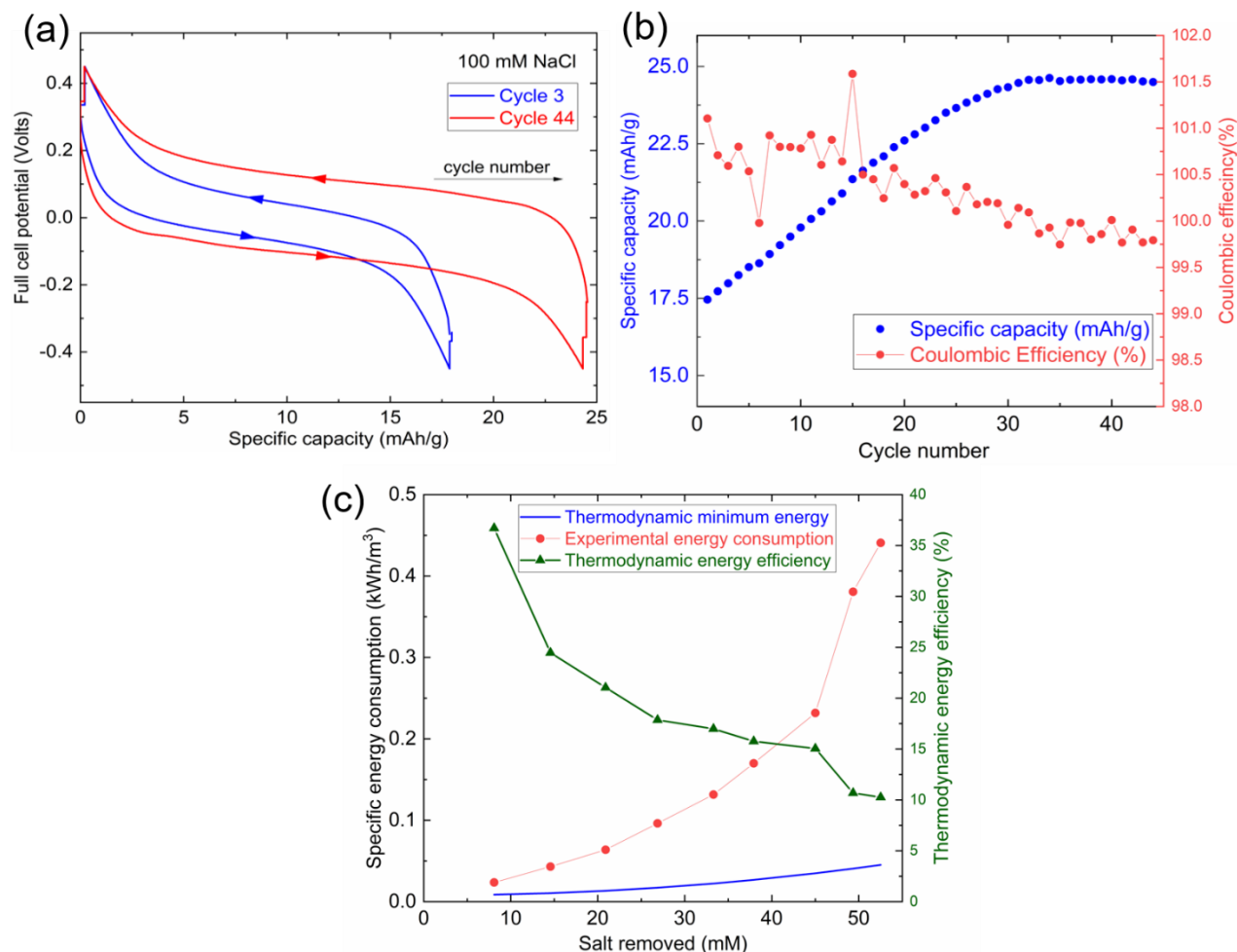


Figure 4.11: Galvanostatic cycling and desalination performance of NTVP electrodes in FDI cell in 100 mM NaCl with (a) cell potential vs specific capacity, (b) specific capacity and coulombic efficiency as a function of cycle number, and (c) specific energy consumption and thermodynamic energy efficiency as a function of salt removed, at a current density of $1\text{mA}/\text{cm}^2$ ($\sim 3\text{C}$ rate) and flow rate of $1\text{ mL}/\text{min}$, and 5 mL of solution in inlet and outlet reservoirs each.

The thermodynamic minimum energy consumption was calculated using equations derived in previous CDI literature¹³⁸ and compared to the total energy consumption of the experimental cell. As evidenced from Fig. 4.11 (c), while 52 mM salt removal could be achieved (calculated from conductivity of inlet and outlet solutions) energy consumption

was an order of magnitude higher for the device (0.44 kWh/m^3 for 50 mM salt removal) compared to the corresponding thermodynamic minimum (0.045 kWh/m^3). This energy consumption of $30 \text{ kJ/mol-salt removed}$ (or 0.44 kWh/m^3) is also nearly 4 times higher than the energy consumption exhibited by PBAs for desalination of 100 mM NaCl at similar current density and salt removal rates.¹³⁹ The poor electrochemical performance can be attributed to several issues encountered during fabrication and operation with NTVP electrodes:

- i) Poor capacity utilization: As seen in Fig. 4.11 (a), the electrodes exhibited only 38 to 55% of total capacity utilization during operation, although with close to 100% coulombic efficiency (Fig. 4.11(b)). Moreover, a peculiar trend of increasing specific capacity achieved with increasing cycling number was observed, discussed later in this section.
- ii) Low overall capacity of electrodes: The FDI cell was designed to operate with electrodes that are at least $150 \text{ }\mu\text{m}$ thick. However, to avoid cracking of the NTVP electrodes, typically only $100\text{-}120 \text{ }\mu\text{m}$ thick electrodes could be made, which restricted the total capacity and hence rate of desalination. The experiment in Fig. 4.11 had electrodes with only $\sim 6.9 \text{ mg/cm}^2$ mass loading of active material, whereas typically $10\text{-}11 \text{ mg/cm}^2$ loading for PBA electrodes was used to achieve appreciable desalination performance.¹³⁹

To make thicker electrodes, overall percentage of binder was increased from 10 to 15%, resulting in electrode composition of 80:5:15 for active: Ketjenblack: PVDF binder, instead of 85:5:10 as described in section 2.2.3. These electrodes were tested in mixed ion solutions to test the level of selectivity achievable by NTVP electrodes operating

continuously in the FDI device. These electrodes had an active material loading of ~ 9.6 mg/cm^2 , approx. $150\ \mu\text{m}$ thickness (although it was non uniform, with a roughness of 10-20 μm), and porosity of 80 to 90%.

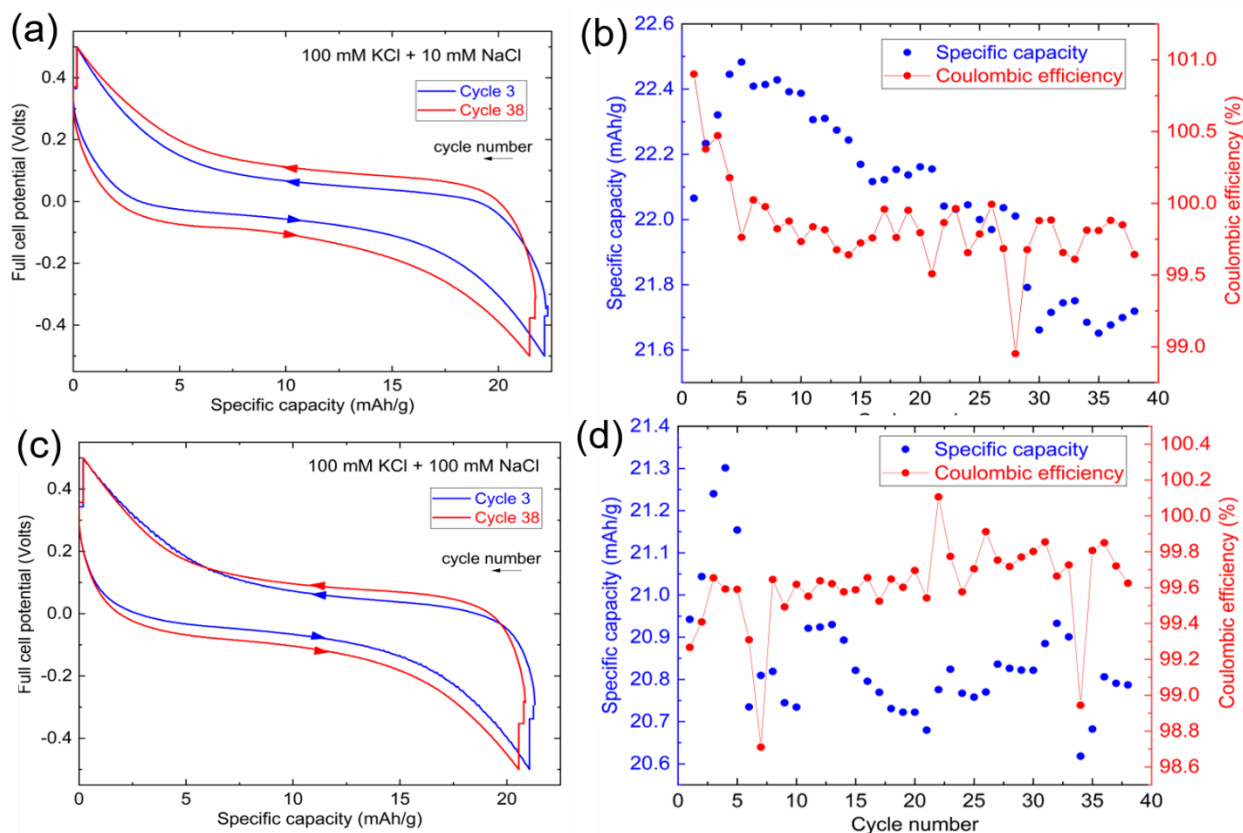


Figure 4.12: NTPV electrodes with 80:5:15 active:KB:binder tested in ternary electrolyte with K^+ and Na^+ cations. (a) Potential vs specific capacity, and (b) specific capacity vs coulombic efficiency in 100 mM KCl+10mM NaCl. (c) and (d) are same galvanostatic cycling parameters in 100 mM KCl + 100 mM NaCl. Flow rate of 0.5 mL/min and current density of $1\ \text{mA}/\text{cm}^2$ ($\sim 2.5\text{C}$) are applied in both experiments.

Fig. 4.12 shows galvanostatic performance of electrodes with higher binder percentage in 100 mM KCl + 100 mM NaCl, and 100 mM KCl + 10 mM NaCl, at a current density of $1\ \text{mA}/\text{cm}^2$ ($\sim 2.5\text{C}$) and flow rate of 0.5 mL/min. The electrodes still achieve only 50% capacity utilization with a coulombic efficiency close to 100%, in both cases, even though they show a specific capacity of between 40 to 45 mAh/g in the flooded cell setup.

Further, in several repeat fabrications, it was found that it is difficult to reliably reproduce the same thickness and active loading. Electrodes tend to crack at higher thicknesses or dry down to 100 to 120 μm . Moreover, in several experiments, it was observed that the anion exchange membrane has a yellowish stain, indicating vanadium dissolution from the active material (Fig. 4.12).

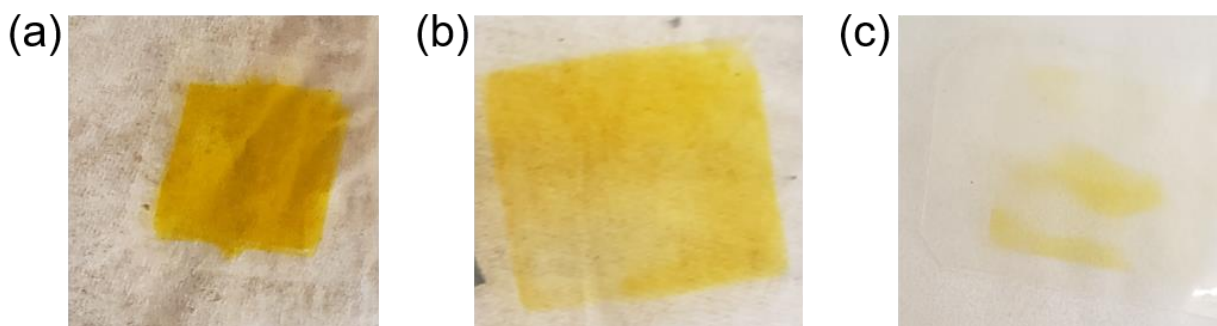


Figure 4.13: Yellowish staining of the anion exchange membrane observed after various experiments in the FDI device using NTVP electrodes with 15% binder. (a) and (b) were observed after long term operation in 100 mM KCl + 10 mM NaCl, and (c) was observed after operation in 100 mM NaCl.

These issues with poor capacity utilization and vanadium dissolution observed in some cases need to be addressed to enable successful desalination and selective cation removal from mixed ion solutions using NTVP. Given the substantial discrepancy in the specific capacities observed for individual electrodes in the flooded cell setup compared to the full cell in the FDI device, it can be deduced that the contrasting geometry of the setups induces different performances of the electrodes. Following reasons are hypothesized for these results:

- 1) NTVP/C particles are coated with a layer of carbon, which makes them hydrophobic. Therefore, wetting the electrodes uniformly throughout their thickness can be a challenge, especially in the FDI device which has an internal volume of only 0.1mL, whereas the flooded cell is a 'semi-infinite' configuration

with 100mL electrolyte. Particularly, the interface between the AEM and hydrophobic particles of NTVP/C in the porous electrode, can be poorly wetted. Therefore, during galvanostatic operation, the overall potential of the electrodes can be driven to extreme values much more quickly before complete capacity is utilized, because of particles at the electrode/AEM interface reaching higher potentials compared to the rest of the bulk. Moreover, this effect was enhanced when the PVDF binder concentration was increased from 10 to 15%, after which yellowish staining of the AEM was seen indicating vanadium dissolution. Vanadium in NTVP would dissolve only when the active particles are driven to extreme potentials.¹¹² Considering that PVDF is also hydrophobic, it can make it more difficult to properly wet the particles, especially at the interface of the electrode and AEM. Further, this problem can be aggravated by binder segregation, which is commonly observed in graphite anodes for Li-ion batteries.^{140,141} During drying, the PVDF binder does not distribute uniformly throughout the thickness of the electrode, but instead higher amount of binder migrates to the surface of the electrode, away from the current collector. This binder concentration difference can be up to three times higher at the top layer compared to the bottom layer near the current collector.^{140,141} Therefore, this effect can further enhance the impedance of the electrode towards the top layer, leading to potential gradients throughout the thickness of the electrode (Fig. 4.14). This hypothesis is further supported by the observation that in experiments with electrodes containing 15% binder, only AEM was stained yellow because of vanadium dissolution, but no such discoloration of the electrolyte was found. This likely implies that the particles at or

near the electrode/AEM interface are reaching higher potentials, but the same is not true for the bulk of the electrode, and that PVDF concentration also plays an important role in the overall wetting and impedance of the electrode.

- 2) Non uniform thickness and roughness of the cast electrodes can lead to capacity and impedance mismatch between the two electrodes, driving the lower capacity or higher impedance electrode to higher potentials, inducing vanadium dissolution in the extreme case.

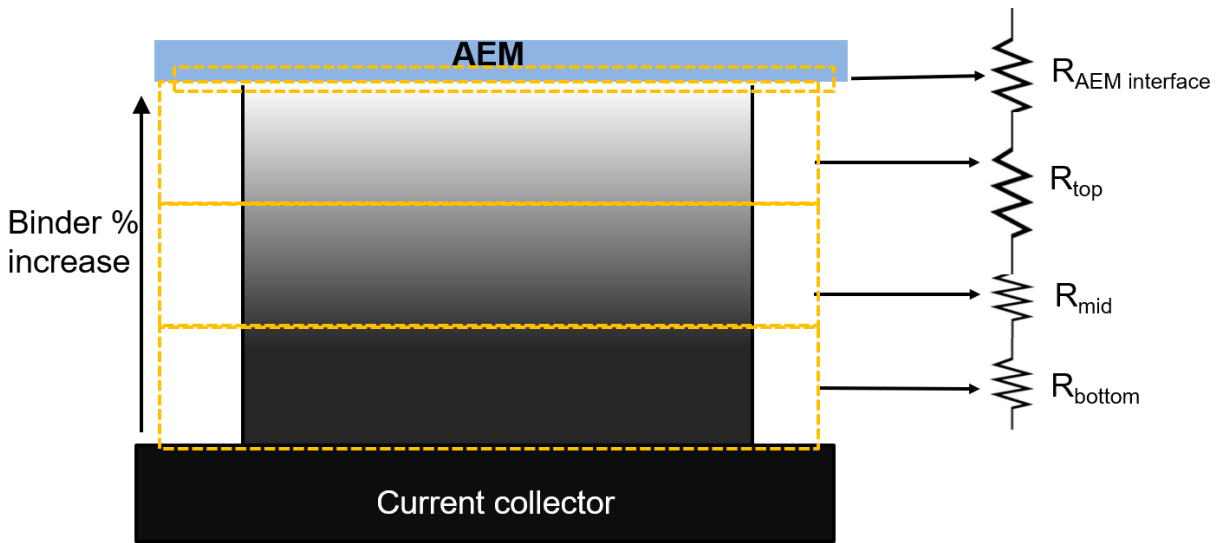


Figure 4.14: Binder migration towards the surface of the electrode can increase resistance at the electrode-AEM interface and upper layer of the electrode, i.e., $R_{\text{AEM interface}}$, $R_{\text{top}} > R_{\text{mid}}$, R_{bottom} , inducing potential gradients across the electrode thickness and over(dis)charging across higher impedance regimes during galvanostatic cycling.

Therefore, a robust fabrication process for porous NTPV electrodes needs to be devised, which ensures uniform thickness of the cast electrode, proper wetting of particles throughout the bulk and electrode/AEM interface, and a low total impedance.

4.7: Summary of findings for using NASICON in Faradaic deionization

Sodium vanadium phosphate (NVP) is theoretically very attractive for desalination of highly saline water, due to its high volumetric and gravimetric charge storage capacity. Moreover, NVP particles can be easily synthesized with a carbon coating, greatly enhancing electronic conductivity of porous electrodes. However, it is plagued by vanadium dissolution during charging in aqueous solutions, leading to complete capacity fade in the first cycle and rendering it unsuitable for FDI in aqueous solvents. Alloying NVP with Ti can lead to substantial improvement in its stability. NTVP, i.e., 50% Ti substituted in NVP exhibits minimal degradation in capacity while maintaining a volumetric charge capacity similar to NiHCF. Equilibrium potential studies show that Na^+ insertion into NTVP follows a solid-solution reaction, in contrast to NVP which undergoes phase separation during intercalation of Na^+ ions. The equilibrium potential profile of NTVP can be modelled effectively using a regular solution model for mixing of two species, giving an interaction parameter (Ω) of $0.57k_B T$, which is higher than that for PBAs ($\Omega \sim 0$). Other alkali and alkaline earth cations were also tested for intercalation into PBAs, and only Li^+ is found to intercalate into NTVP, with a 33% lower capacity at a 70 mV lower standard reduction potential than Na^+ insertion. Therefore, NTVP is 16 times more selective for Na^+ over Li^+ at equilibrium. Selectivity sequence of $\text{Na}^+ \gg \text{Li}^+ \gg \text{K}^+$, Mg^{2+} , Ca^{2+} was observed for NTVP. A minimum selectivity ratio of 56.6 was established for porous electrodes of NTVP, for capturing Na^+ over K^+ and other ions, taking the maximum amount of non-intercalating cations that can be capacitively adsorbed into the electric double layers of the electrode. Porous electrodes of NTVP were further tested in a FDI cell, for testing desalination and selective intercalation performance. A poor

capacity utilization of ~50-60% was observed, mechanisms for which were hypothesized.

A robust electrode fabrication process ensuring uniform thickness, proper wetting of particles throughout the electrode, including the interface of AEM/electrode needs to be devised to maximize performance.

Overall, NTVP can prove to be an impactful material with applications across several domains, ranging from desalination, selective removal for saline agriculture and purification processes in chemical manufacturing.

Chapter 5 : Faradaic deionization materials for carbon dioxide capture

5.1: Rising need and challenges for capturing carbon dioxide from air

The past decade recorded 100 to 200 times higher rate of growth of CO₂ in the atmosphere compared to what the earth experienced during the transition from the last ice age.¹⁴² Rapid burning of fossil fuels for energy and manufacturing since the industrial age has significantly contributed to the global climate change crisis. Presently, even an immediate and complete transition to renewable energy sources alone will not be enough to mitigate this calamity. Non-fossil fuel-based energy sources (solar, wind, hydropower, and nuclear) account for <15% of the global primary energy consumption today, while >80% primary energy demand is met by fossil fuels (coal, oil, natural gas).¹⁴³ Practically, it will take a significant amount of time (over two decades) to completely transition the global economy to clean energy sources, and curb the global average temperature rise to <2°C. Therefore, drastic steps need to be taken along with the massive undertaking already underway in transitioning our economies towards renewables. Consequently, there is an urgent need to achieve negative CO₂ emissions in a sustainable and economic manner in the next two decades.

In principle, to capture CO₂ from atmospheric air at a large scale, economic feasibility of three steps needs to be achieved: Carbon dioxide capture from air (with ~400 ppm CO₂, global average), storage of captured CO₂, and/or conversion of stored/captured CO₂ into useful products. If even one of these steps is expensive, it will be difficult to make carbon capture a reality. Therefore, carbon capture, storage and conversion technologies have received tremendous research interest in the past decade. This work focusses on carbon capture aspect of the problem.

Current state-of-the art direct air CO₂ capture process consumes nearly 10 to 12 times more energy (210-240 kJ/mol CO₂) than the thermodynamic minimum (~20 kJ/mol CO₂).^{144,145} Consequently, a levelized cost of capture going up to 94 to 232 \$/t CO₂ has been achieved,¹⁴⁵ which is only marginally lower than the cost for introducing CO₂ in the atmosphere by vehicular burning of gasoline (~250-300 \$/t CO₂ based on current fuel prices).

Therefore, alternate approaches with appreciably lower capital and energy costs can dramatically improve the economics of CO₂ capture by enabling profitable conversion of the captured CO₂ to fuels or valorized products.

5.2: pH-swing electrochemical CO₂ capture

With the development of faradaic deionization technology in the past few years, a new electrochemical pathway has emerged for capturing CO₂ from air, flue gas emissions and other sources. Several recent efforts have proposed leveraging the pH-dependent solubility of CO₂ gas to capture CO₂ from dilute sources (such as 400 ppm CO₂ present in atmosphere or 0.1 bar CO₂ from flue gas). CO₂ dissolves as carbonate and bicarbonate ions in water, and its solubility increases with increasing pH.¹⁴⁶ Therefore, an appreciable change in pH of the feed stream containing dissolved CO₂ can be used to obtain pure CO₂ gas, by shifting pH from higher to lower values. While earlier attempts used electrodialysis stacks to split water (containing dissolved CO₂) at metal electrodes to modulate the pH¹⁴⁷, their feasibility was prohibited due to large energy consumption involved in the process. On the other hand, membrane capacitive deionization using symmetric carbon electrodes to absorb/desorb H⁺ and HCO₃⁻ ions is primarily limited by the low charge storage capacity in the electric double layer.¹⁴⁸

More recently, FDI architectures have been proposed wherein pH cycles between near neutral and acidic regime, employing materials with higher charge storage capacity which can appreciably change pH of the electrolyte within a moderate potential window of operation. Various compounds have been proposed for reversible (de)acidification of the electrolyte, such as phenazine based organic molecules that undergo proton coupled electron transfer reactions (PCET)¹⁴⁶ and MnO₂ electrodes for proton (de)intercalation.¹⁴⁹

5.2.1 Alkaline based CO₂ capture

While the recent FDI approaches to CO₂ capture improve upon previous electrochemical approaches, the rate of CO₂ removal and is still limited due to operation in the pH ~ 1 to 8. Figure 5.1 shows the pH dependent solubility of CO₂(g). Solutions with initial pH varying from 0 to 15 were modeled, and the total dissolved inorganic carbon (DIC), i.e., ([HCO₃⁻] + [CO₃²⁻]) and ratio of bicarbonate and carbonate anions is plotted as a function of final pH after complete dissolution of CO₂, at equilibrium. The detailed equations used for these calculations along with the values for chemical equilibrium constants are described in Appendix D. As evidenced from Fig. 5.1, CO₂ is >5 orders of magnitude more soluble in alkaline electrolytes, compared to neutral and acidic media. A large pH swing in the near the neutral to acidic regime will only change DIC by ~ 2 μmol/L, whereas a similar pH swing in alkaline regime (say from 11 to 9) will change DIC by 2 mol/L, more than six orders of magnitude higher than the acidic operation. That is why chemical approaches for carbon capture developed in industries use highly alkaline electrolyte (>4M KOH) to dissolve CO₂.¹⁴⁵

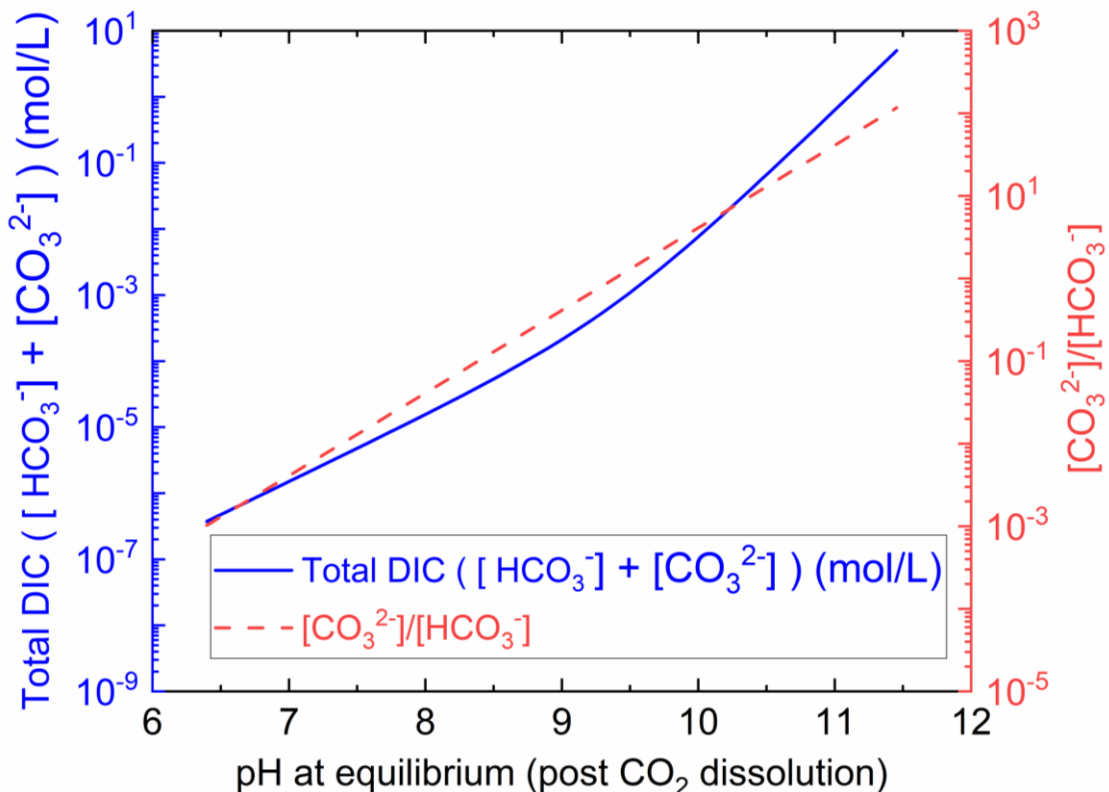


Figure 5.1: Total dissolved inorganic carbon (DIC) and $[\text{CO}_3^{2-}]/[\text{HCO}_3^-]$ as a function of final pH obtained after complete dissolution of $\text{CO}_2(\text{g})$, at equilibrium.

To enable FDI for alkaline based CO_2 capture, materials that can reversibly (de)insert OH^- ions are required. Nickel hydroxide/oxyhydroxide redox couple can prove suitable for this purpose, since this material is already deployed commercially in rechargeable Nickel-metal hydride (NiMH) batteries, which use highly basic electrolyte (~ 5 to 6 M KOH).^{150,151} $\text{Ni}(\text{OH})_2/\text{NiOOH}$ undergoes the following reversible reaction in alkaline media:

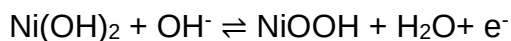


Fig. 5.2 shows a schematic for an FDI device using symmetric $\text{Ni}(\text{OH})_2/\text{NiOOH}$ electrodes separated by a cation exchange membrane (CEM) to capture/release OH^- ions during cycling.

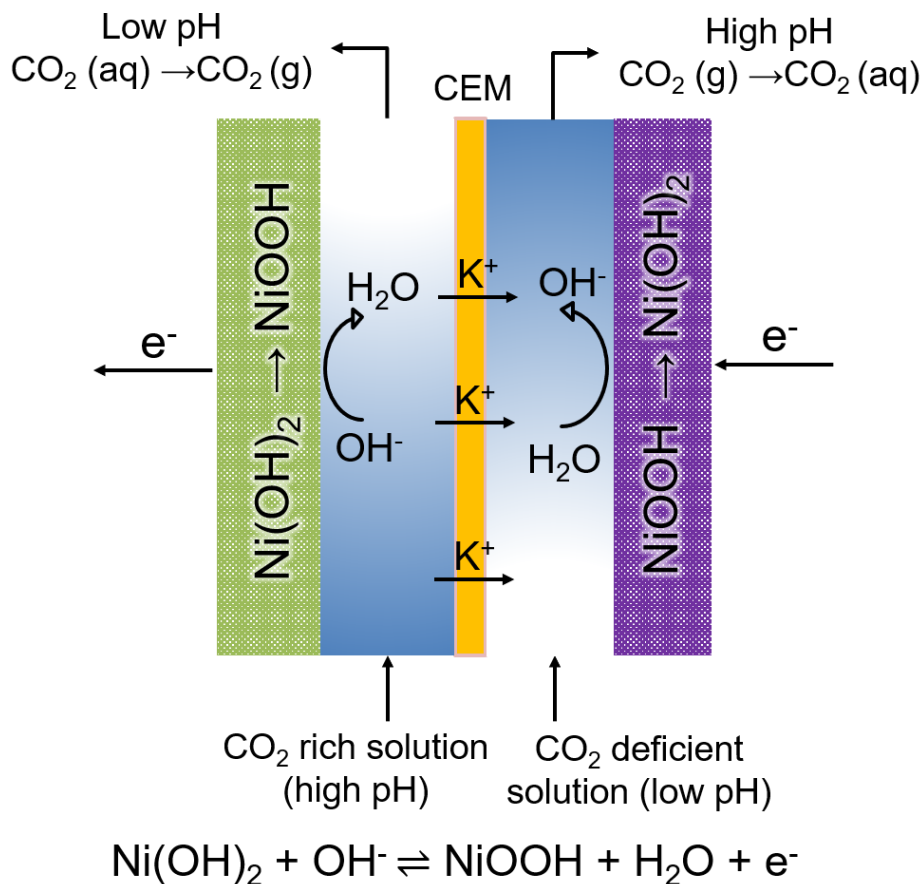


Figure 5.2: FDI device schematic for symmetric Nickel hydroxide electrodes for collecting CO_2 dissolved in alkaline electrolyte by modulating pH of feed streams separated by a cation exchange membrane (CEM).

The high pH solution flown through the Ni(OH)_2 electrode has larger concentration of dissolved CO_2 in the form of carbonates and bicarbonates. When the pH is reduced during oxidation of Ni(OH)_2 , the CO_2 dissolution equilibrium shifts to release $\text{CO}_2(\text{g})$ at the outlet, due to lower solubility of $\text{HCO}_3^-/\text{CO}_3^{2-}$. The reverse phenomenon happens for the CO_2 deficient stream flown through the NiOOH compartment, which gets concentrated with OH^- ions during the reduction of NiOOH , and hence dissolves more $\text{CO}_2(\text{g})$ as (bi)carbonate ions. These streams are switched in the next cycle to repeat the process and capture more CO_2 . Note that CO_3^{2-} ions become the major charge carriers at high pH instead of OH^- ions (at equilibrium) (Fig. 5.1), which necessitates stable operation of

active material in electrolytes with a mixture of OH^- and CO_3^{2-} ions. In this preliminary work, $\text{NiOOH}/\text{Ni}(\text{OH})_2$ couple is first tested in alkaline electrolytes, which will later be followed by more rigorous testing in mixed electrolytes with OH^- , HCO_3^- and CO_3^{2-} ions. In principle $\text{Ni}(\text{OH})_2/\text{NiOOH}$ exist in three phases – α , β and γ . The Bode reaction scheme^{152,153} shows the relevant reactions connecting these phases. The β/β couple is reversible, but β irreversibly transforms to γ on overcharging. Also, α converts to β phase on ageing in alkaline solutions.^{152,153} However, only the β/β redox couple and α , γ couples are known to be reversible, with the β/β couple being the preferred one due to its high stability and reversibility. α - $\text{Ni}(\text{OH})_2$ undergoes transition to the β phase when aged in aqueous alkaline electrolytes.¹⁵³ Nickel hydroxide electrodes also exhibit a very high gravimetric charge storage capacities between 135 to 250 mAh/g and volumetric capacity of up to 550 mAh/cm³ in 6M KOH^{151,154,155} which can prove especially useful for inducing large pH swings in alkaline electrolytes.

5.3: Characterization of $\text{Ni}(\text{OH})_2$ / NiOOH electrodes

While $\text{Ni}(\text{OH})_2$ has been actively studied as a cathode material in rechargeable batteries, it hasn't been tested in a dynamic environment as an FDI cell, where pH would change dramatically during (dis)charging, and other ions such as carbonates and bicarbonates will be present in the electrolyte. Therefore, a fundamental understanding needs to be developed on rate capability, stability and degradation mechanisms of $\text{Ni}(\text{OH})_2$ electrodes, in the conditions for the FDI cell. Consequently, electrochemical characterization was performed on slurry casted electrodes made with $\text{Ni}(\text{OH})_2$ synthesized by coprecipitation in the lab, as well as commercial $\text{Ni}(\text{OH})_2$ electrodes obtained by disassembling NiMH batteries.

5.3.1 Synthesis of β -Ni(OH)₂ electrodes

β -Ni(OH)₂ powders were synthesized following a coprecipitation method as described in literature.¹⁵¹ 70 mL of 0.4 M Ni(NO₃)₂·6 H₂O (Sigma-Aldrich) in DI water was added dropwise at a rate of 2-3 mL/min (using a burette) to 70 mL of 1M NaOH (aq) at 45°C, under vigorous stirring. After completing the dropwise addition, the green dispersion was aged at 75°C for 12h, while vigorously stirring throughout. The final mixture was centrifuged several times to obtain Ni(OH)₂ particles, which were washed copiously with DI water till pH of the supernatant liquor was reduced to 7. The crystal structure of the particles was characterized using X-ray diffraction (Bruker, D8), and found to be in good agreement with literature. The as-synthesized Ni(OH)₂ powders formed a hexagonal lattice, with P-3m1 space group and lattice parameters of 3.12 Å and 4.61 Å.¹⁵⁶

Electrode slurries were made using the same procedure as described for unmilled electrodes in section 2.2.1. Active material, ketjenblack conducting additive, and PVDF binder were in the ratio of 85:5:10. The slurry was casted onto graphite current collectors and dried overnight in the fumehood. Final electrodes obtained were ~ 90µm thick, with an active material loading of 7-8 mg/cm².

5.3.2 Electrochemical characterization of lab synthesized β -Ni(OH)₂

Electrodes were characterized in a flooded cell setup in 2M KOH exposed to air at ~20°C, with Hg/HgO reference (0.014V vs SHE) and a large, activated carbon counter electrode. As evidenced from Fig. 5.3 (a) and (b), the charge and discharge profiles are in complete contrast to each other. The coulombic efficiency for this material is less than 50%, with the capacity decreasing as cycling progresses. The charging potential lies above the

equilibrium potential line O₂ evolution (actual potential would lie lower, since O₂ is only at 0.2 bar in the lab atmosphere).

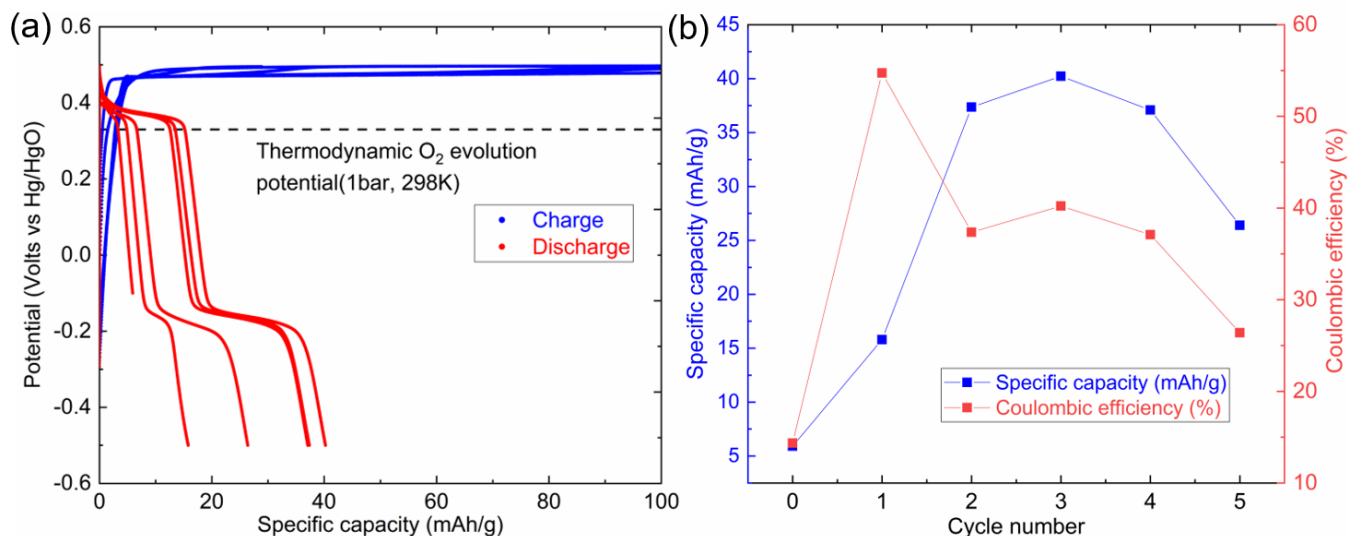


Figure 5.3: Galvanostatic cycling performance of lab synthesized β -Ni(OH)₂, with (a) variation of potential vs specific capacity, and (b) specific capacity and coulombic efficiency as a function of number of cycles.

There are largely three mechanisms known for the low coulombic efficiency and fast capacity degradation¹⁵⁵:

- i) Competition with O₂ evolution: Ni(OH)₂ is an extensively studied oxygen evolution catalyst. Therefore, during charging, especially in a flooded cell where no oxygen buildup occurs to saturate the O₂ content in the electrolyte, O₂ evolution can continuously take place.
- ii) Loss of active material during charging: During the phase transition of β -Ni(OH)₂ to β -NiOOH during charging, volume expansion > 200% can occur, which can lead to loss of contact of the active material with the current collector and conducting network.

- iii) Irreversible phase transition to γ -NiOOH: When β -Ni(OH)₂ is overcharged, it can partially transform irreversibly into γ -NiOOH, which is electrochemically inactive.

Further, the existence of two plateaus during discharge (Fig. 5.3 (a)) likely results from the complex electronic structure differences in the two phases. β -Ni(OH)₂ is a p-type semiconductor with a bandgap of 3.7 eV, whereas β -NiOOH is an n-type semiconductor with a bandgap of 1.7 eV.¹⁵⁵ During discharge, the p-type nature of Ni(OH)₂ can start dominating, and holes can become the primary charge carriers. This change in composition of charge carriers can lead to formation of a Schottky barrier(s) between the current collector and active material and the conducting additive and active material.¹⁵⁵ Given the poor electrochemical performance by lab synthesized β -Ni(OH)₂ powders, commercial electrodes from NiMH batteries were characterized.

5.3.3 Electrochemical characterization of commercial Ni(OH)₂ electrodes

Rechargeable NiMH batteries were purchased (EBL, 2800 mAh) for disassembly. Each battery was galvanostatically discharged at a rate of C/10 to 0% SOC (state-of-charge) before opening. EDXRF was done for measuring composition of these electrodes. Table 5.1 shows that these commercial electrodes are doped with 7% Co and 4 % Zn. Co and Zn doping are typically employed to improve charge retention and prevent capacity fade of NiMH batteries.¹⁵⁵ Further, nickel foam is used as a current collector with the active material impregnated throughout the foam, adhering strongly to it. Consequently, attempts to scrape the active material from the current collector result in insignificant quantity of powders being detached, or breakdown and cracking of the electrode if excessive force was applied. Therefore, the electrode pieces were tested as obtained

after disassembly. Approximate longitudinal cross section area of these pieces was 2 cm². A flooded cell exposed to air at ~20°C with 2M KOH electrolyte, Hg/HgO (2M KOH) reference and a large, activated carbon counter electrode was again used as the test setup.

Element	Relative % by wt.
Nickel	87.57
Cobalt	7.53
Zinc	4.74
La	0.157

Table 5.1: EDXRF of Ni(OH)₂ electrodes (post discharge) from commercial NiMH batteries (EBL)

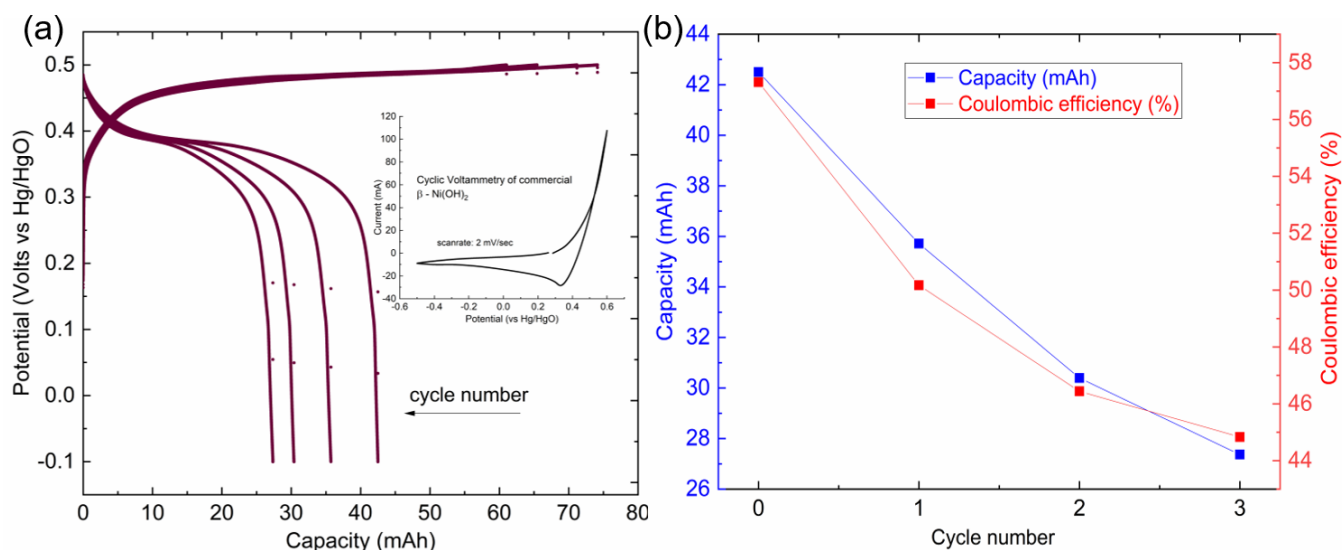


Figure 5.4: (a) and (b) Galvanostatic cycling performance of commercial Ni(OH)₂ electrode in 2 M KOH, with Hg/HgO reference and large AC counter. Inset in (a) shows cyclic voltammetry of the electrode at 2 mV/sec.

Galvanostatic cycling of commercial Ni(OH)₂ electrodes in 2 M KOH (Fig. 5.4 (a) and (b)) also exhibited capacity fade with a low coulombic efficiency (~50%) when tested in the flooded cell when the maximum charging potential was set to 0.5 V vs Hg/HgO. However,

only a single discharge plateau was observed, and the cyclic voltammetry (CV) plot (inset, Fig. 5.4(a)) also showed one discharge peak till -0.5V vs Hg/HgO. There was also no oxidation peak observed in the CV, likely due to phase transition of Ni(OH)_2 to NiOOH being convolved with O_2 evolution. Note that a major difference in testing commercial Ni(OH)_2 electrodes in the flooded cell compared to their operation in a tightly sealed enclosed cell lies in the buildup of O_2 partial pressure. Tightly enclosed cells have very small amount of electrolyte per unit volume of active material and can also saturate with O_2 after a small amount of the gas is evolved. However, the same is not true in this setup, where there is a large amount of electrolyte compared to the active material, and O_2 partial pressure remains almost constant around 0.2 bar.

Considering the low coulombic efficiencies being obtained with both lab synthesized and commercial Ni(OH)_2 powders, a potential window needs to be established for stable operation of a symmetric configuration of Ni(OH)_2 electrodes (Fig. 5.2). The subsequent tests were performed in a similar flooded cell as the previous tests, but in a symmetric flooded cell configuration, with both working and counter electrodes as commercial Ni(OH)_2 electrodes. The batteries were galvanostatically discharged to 50% SOC instead of 0% before disassembling them to obtain electrodes. The potential difference between the working and counter electrodes was controlled, and potential of each was measured with respect to Hg/HgO reference.

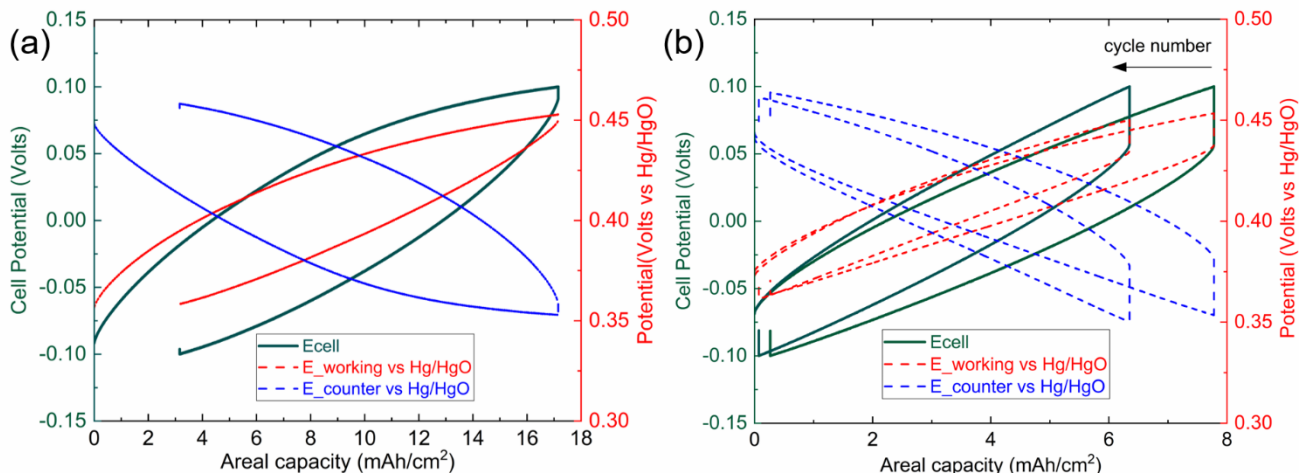


Figure 5.5: Galvanostatic cycling of symmetric flooded configuration of commercial Ni(OH)_2 in 2M KOH, cycled within a cell potential range of -0.1V to 0.1V (green). (a) Performance with 2.5 mA /cm² and (b) 10 mA/cm² applied current density (normalized to longitudinal cross section area of ~2cm²)

Fig. 5.5 shows the galvanostatic cycling of the symmetric flooded cell configuration in 2M KOH for the commercial Ni(OH)_2 electrodes (longitudinal cross section $\sim 2 \text{ cm}^2$). The capacity seems much more stable now, with the cell cycled at 10 mA/cm² having half the capacity compared to running the cell at 2.5 mA/cm². However, the coulombic efficiency $> 90\%$ for the cells cycled at 10 mA/cm², with much slower drop in capacity. Given the small potential window of operation, it is important to estimate the contribution from double layer capacitance, to make sure that faradaic reactions for reversible OH^- capture contribute the major fraction of specific capacity. If it is assumed that the area specific electric double layer capacitance of the 2M KOH electrolyte and Ni(OH)_2 electrode interface is an exorbitantly high value of $100 \mu\text{F}/\text{cm}^2$ (more realistic estimates vary from 3 to $4 \mu\text{F}/\text{cm}^2$ to 30 to $40 \mu\text{F}/\text{cm}^2$),¹⁵⁷ and assuming a high surface area of $85 \text{ m}^2/\text{g}$ (as specified by manufacturers) for nano Nickel-oxyhydroxide powder,¹⁵⁸ the total double layer capacitance contribution within this 0.2V potential range will be 4.7 mAh, which is $<50\%$ of the total measured capacity (Fig. 5.5). A more realistic estimate of the double layer capacitance contribution would be between from 0.2 to 2 mAh, based on

experimentally determined values of specific capacitance in such alkaline electrolytes, which is between 2 to 20% of the measured charge capacity.¹⁵⁷

Considering that Ni(OH)_2 has always majorly been explored with KOH electrolyte in literature, the commercial electrodes were also tested in 2M NaOH, to understand if the nature of the cation causes any difference in performance. Successfully using NaOH can also prove beneficial for an asymmetric FDI cell, with one electrode as OH^- capturing Ni(OH)_2 and the other one being a cation capturing electrode stable in alkaline electrolytes, such as $\text{Na}_2\text{Ti(PO}_4)_3$. Fig. 5.6 compares galvanostatic operation of the symmetric flooded configuration in 2M KOH and 2M NaOH electrolytes. No discernible difference was found in the potential profiles or charge storage, at least during short term cycling of ~ 10 cycles. Therefore, these electrodes were further characterized in NaOH electrolyte.

Note that there was still some capacity fade, although at a much slower rate, but with coulombic efficiencies $>90\%$. As discussed earlier, some material was lost due to lack of adhesion to the current collector because of volume expansion during cycling. This loss can be minimized in a sealed cell because active material is tightly pressed against the current collector and electrode.

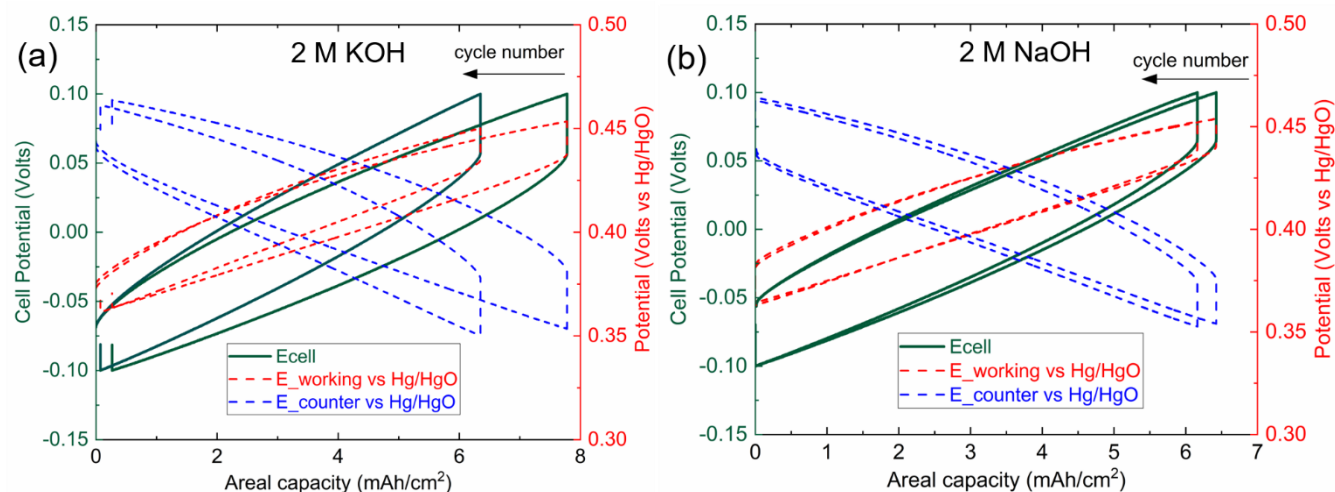


Figure 5.6: Galvanostatic cycling of symmetric flooded configuration of commercial $\text{Ni}(\text{OH})_2$ in (a) 2M KOH and (b) 2M NaOH cycled within a cell potential range of -0.1V to 0.1V, at 10 mA/cm².

Since the electrodes were cycling stably within a potential window of $\pm 100\text{mV}$, the potential range of cell cycling was extended by 50 mV to $\pm 150\text{mV}$, to understand its effect on the increase in areal capacity and cycle life.

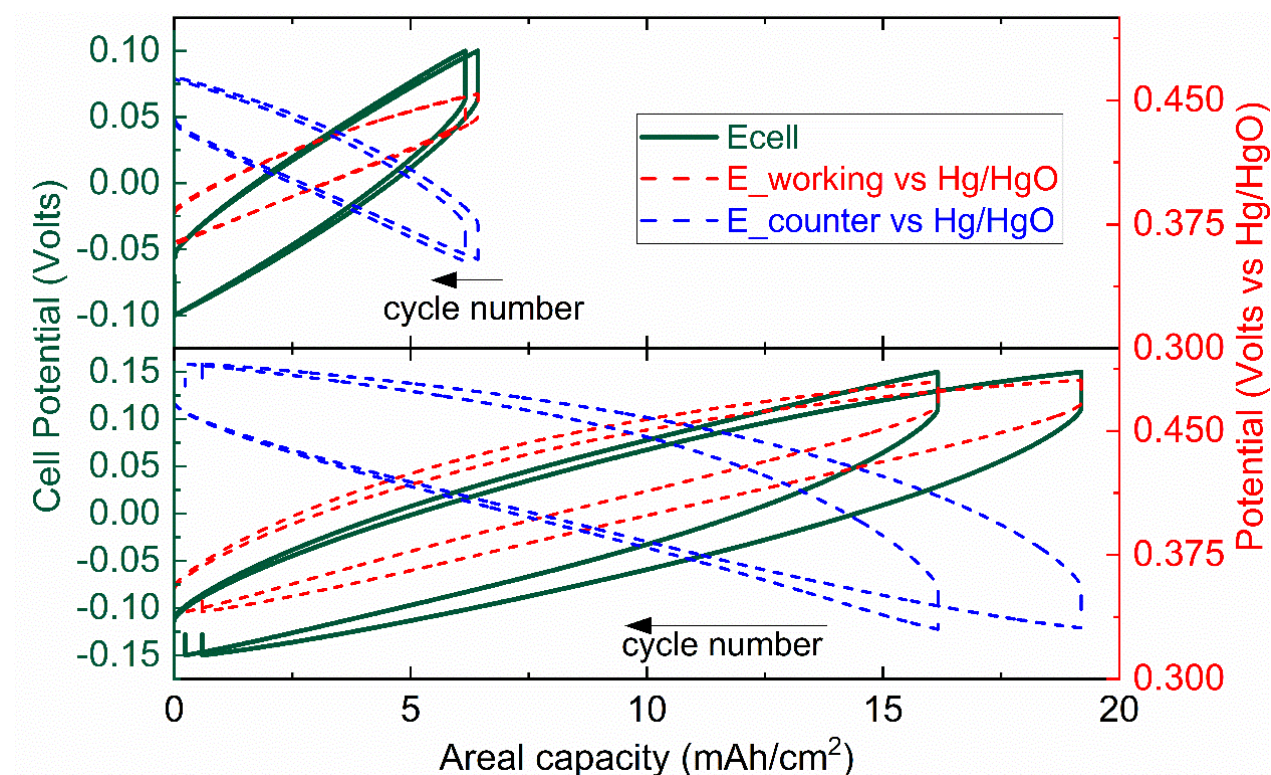


Figure 5.7: Comparing galvanostatic cycling of symmetric flooded configuration of commercial $\text{Ni}(\text{OH})_2$ electrodes in 2M NaOH between -0.1V to 0.1V, and -0.15V to 0.15V at 10 mA/cm².

Increasing the potential window of operation by 50 mV increases areal capacity by three-fold, from 5 mAh/cm² to 15 mAh/cm² (Fig. 5.7).

Since the electrodes are stable in 2M NaOH at 10 mA/cm², in a potential range of -0.15V to 0.15V, their rate capability was tested by applying higher current densities.

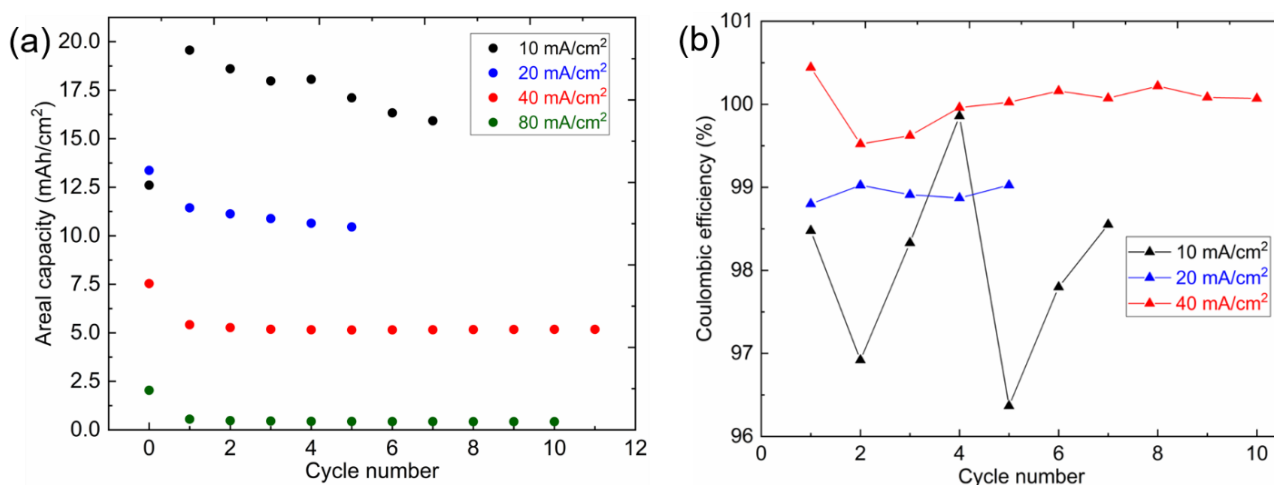


Figure 5.8: Rate capability of commercial Ni(OH)₂ in a symmetric flooded cell configuration in 2M NaOH. (a) Specific capacity as a function of cycle number, and (b) coulombic efficiency vs cycle number for current densities from 10 mA/cm² to 80 mA/cm².

With every doubling of current starting from 10 mA/cm², the areal capacity drops by 40%. The coulombic efficiencies increase with increasing current and are found in the range of 96 to 100%, while the capacity fade is slowed at higher currents. The high coulombic efficiencies indicate that O₂ evolution is suppressed within this potential range, especially at higher C-rates.

5.4 Summary of preliminary findings for using Ni(OH)₂ in alkaline FDI

FDI based CO₂ capture using an alkaline medium offers a substantial improvement over existing designs proposing use of acidic and neutral media, provided the appropriate materials are found for use in the dynamic alkaline environment of such a device. While Ni(OH)₂ has been extensively used in alkaline supercapacitors and batteries, it is used in

relatively static environments with very high concentration of electrolyte (e.g. 6M KOH). Therefore, Ni(OH)_2 from two sources, i.e., synthesized using coprecipitation process at the lab, and disassembled from commercial NiMH batteries was characterized in alkaline electrolytes. The lab synthesized Ni(OH)_2 powders were incorporated into slurry casted porous electrodes on flat graphite current collectors. These electrodes performed poorly, yielding a low specific capacity, <50% coulombic efficiency and rapid capacity degradation. Three common failure mechanisms challenge the life of an Ni(OH)_2 electrode – O_2 evolution, loss of adhesion to current collector and irreversible phase transition from β to γ phase due to overcharging. Unlike lab synthesized Ni(OH)_2 , commercial Ni(OH)_2 powders were found to be doped with Co and Zn to improve charge retention. Further, the electrodes were made by impregnating Ni(OH)_2 powders into Ni foam current collectors, resulting in a much stronger adhesion compared to conventional slurry casting on flat current collectors. Therefore, these commercial electrodes were tested in 2M KOH and 2M NaOH, in a flooded cell setup exposed to air. A limited cell potential range of cycling up to -0.15V to 0.15V for a symmetric flooded cell with Ni(OH)_2 electrodes was found to have >95% coulombic efficiency from areal current densities of 10 mA/cm^2 to 40 mA/cm^2 (normalized by longitudinal area of commercial electrodes), in both 2M KOH and 2M NaOH electrolytes. Higher potential range of cycling will lead to higher asymmetry in (dis)charge profiles of individual electrodes. Further testing in different concentrations of electrolytes, varying O_2 partial pressures and in the presence of (bi)carbonate ions will be done to understand the performance limitations of this material in this new FDI concept.

Chapter 6 : Summary of Conclusions

This dissertation explored a range of different materials for use in Faradaic deionization for various applications. While Prussian blue analogues, NASICON and nickel (oxy)hydroxide show completely different physical and electrochemical characteristics, pursuing in depth characterization of these materials helped realize key takeaways for charting the path ahead in the emerging field of FDI.

There is a lot of insight to be gained from materials that have been typically used in energy storage applications and applying it to FDI. While the materials used maybe similar, the challenges encountered in applying them for FDI are completely different. This difference motivates a deeper study of materials that may have been studied for a long time by many researchers, but in a new context. For example, the study of rate limiting mechanisms of NiHCF_e was motivated by the requirement for high-rate capability and enabling fast, energy efficient desalination. In most practical batteries, non-aqueous electrolytes are used, where ionic conductivity in organic electrolytes becomes rate limiting, and electron limited apparent diffusion is not typically encountered. However, this new understanding can now benefit both the emerging fields of FDI and aqueous batteries. Similarly, understanding the degradation mechanisms of NiHCF_e in divalent electrolytes is crucial to FDI compared to other fields like energy storage, where the electrolyte can be modified to suit device performance. Therefore, new fundamental knowledge about NiHCF_e was uncovered, especially because it was being studied for FDI. Likewise, NASICON family of materials has been studied for many decades for use as solid-state electrolyte and electrodes primarily in non-aqueous batteries, and more recently in aqueous ones. However, extending its use in FDI brought about new challenges and opportunities, such

as stabilizing the material in aqueous environments, and specifically exploiting its affinity for Na^+ to obtain electrodes with record selectivity for Na^+ over other cations, which would otherwise have remained unexplored. Lastly, Ni(OH)_2 is probably among the most well studied materials to date, considering more than five decades of research exploring all conceivable aspects. Yet, based on the trend of discovering new knowledge for other materials in this work, using Ni(OH)_2 in a completely different application such as FDI for alkaline CO_2 capture presents an exciting opportunity of unearthing new fundamental understanding as well as making a real world impact on one of the most pressing problems in the world.

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Appendix A : Non-dimensionalization of spherical diffusion equations for finite volume simulations for galvanostatic cycling

Using Fick's second law for transient diffusion in spherical coordinates we have:

$$\frac{\partial x}{\partial t} = \nabla \cdot (D \nabla x) = \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 D \frac{\partial x}{\partial r}). \quad (\text{A1})$$

Here, x is the degree of intercalation, t is time, D_{app} is the apparent diffusion coefficient, and r is the radial position coordinate. We impose a galvanostatic boundary condition that fixes the flux of cations at the surface of the sphere:

$$\frac{i}{AF} = N'' = \mp D \frac{\partial x}{\partial r} \Big|_{r=R} C_{s,max}, \quad (\text{A2})$$

where I is total current, A is the surface area, F is Faraday's constant, N'' is the molar flux of cations, and $C_{s,max}$ the maximum cation concentration within the sphere, and the positive and negative signs correspond to charge and discharge conditions, respectively. Expressing flux in terms of a theoretical charge/discharge time τ_c , which is simply the inverse of the applied C-rate, we have:

$$N'' = \frac{C_{s,max} V}{A \tau_c} = \frac{C_{s,max} R}{3 \tau_c}, \quad (\text{A3})$$

where V and R are the volume and radius of the sphere, respectively. We invoke definitions of dimensionless time $t^* = t/\tau_c$ and dimensionless radial position $r^* = r/R$ to finally obtain non-dimensional versions of Eqs. 1 and 2:

$$\frac{\partial x}{\partial t^*} = \frac{1}{r^{*2}} \frac{\partial}{\partial r^*} (r^{*2} \tau_c \frac{D}{R^2} \frac{\partial x}{\partial r^*}) = \frac{1}{r^{*2}} \frac{\partial}{\partial r^*} (r^{*2} \frac{\tau_c}{\tau} \frac{\partial x}{\partial r^*}) \quad \text{and} \quad (\text{A4})$$

$$\mp 3 \frac{\tau_c}{\tau} \frac{\partial x}{\partial r^*} \Big|_{r^*=1} = 1. \quad (\text{A5})$$

Here, τ is the apparent diffusion time scale given as $\tau = R^2/D_{app}$. From Eqns. A4 and A5 we infer that the degree of intercalation x is function only of dimensionless time t^* and radial position r^* . Hence, explicit knowledge of the radius of the electroactive particle is not required if the dependence of τ as a function of x is known and galvanostatic conditions are imposed.

Appendix B: PITT experimental fitting and error calculations

Experimental diffusion time scales and Biot numbers were obtained by fitting current versus time for times shorter than 1 s to Eq. (1) at each PITT step. Towards the end of both charging and discharging sequences, a drop in fitted diffusion time scales was observed (Figure B1(a) and (b)), which deviates from those fitted at the beginning of the opposing sequence. To check whether this trend is artificial, we compared the variation of the fractional charge transferred with the experimentally obtained response for each PITT step. This comparison gives insight into whether complete charging/discharging has taken place at a potential step, or if there is over(dis)charging due to possible side reactions.

The fractional charge transferred at any PITT step can be obtained by solving the spherical diffusion equation to obtain the concentration distribution in a particle, and subsequently integrating the resulting expression for current over spatial coordinates.⁵² The fractional charge transferred $\Delta Q(t)/\Delta Q_{total}$ is dependent on the Biot number Bi and diffusion time scale τ according to the following equation:

$$\frac{\Delta Q(t)}{\Delta Q_{total}} = -6Bi \sum_{n=1}^{\infty} \frac{\lambda_n \cos(\lambda_n) - \sin(\lambda_n)}{(\lambda_n^2 + Bi^2 - Bi) \lambda_n^2 \sin(\lambda_n)} \left(1 - \exp\left(-\lambda_n^2 \frac{t}{\tau}\right) \right) \quad (B1)$$

where λ_n is the n^{th} root of the transcendental equation $1 - \lambda_n \cot(\lambda_n) = Bi$. The response of fractional charge with time at all steps during the PITT procedure is similar to the theoretically predicted curves (Figure B2(a)) if agglomerates are spherical and NPs within them are homogeneously distributed. However, as shown in Figure B2(b), while most of the PITT steps show this expected response, there is a significant deviation observed during terminal PITT steps.

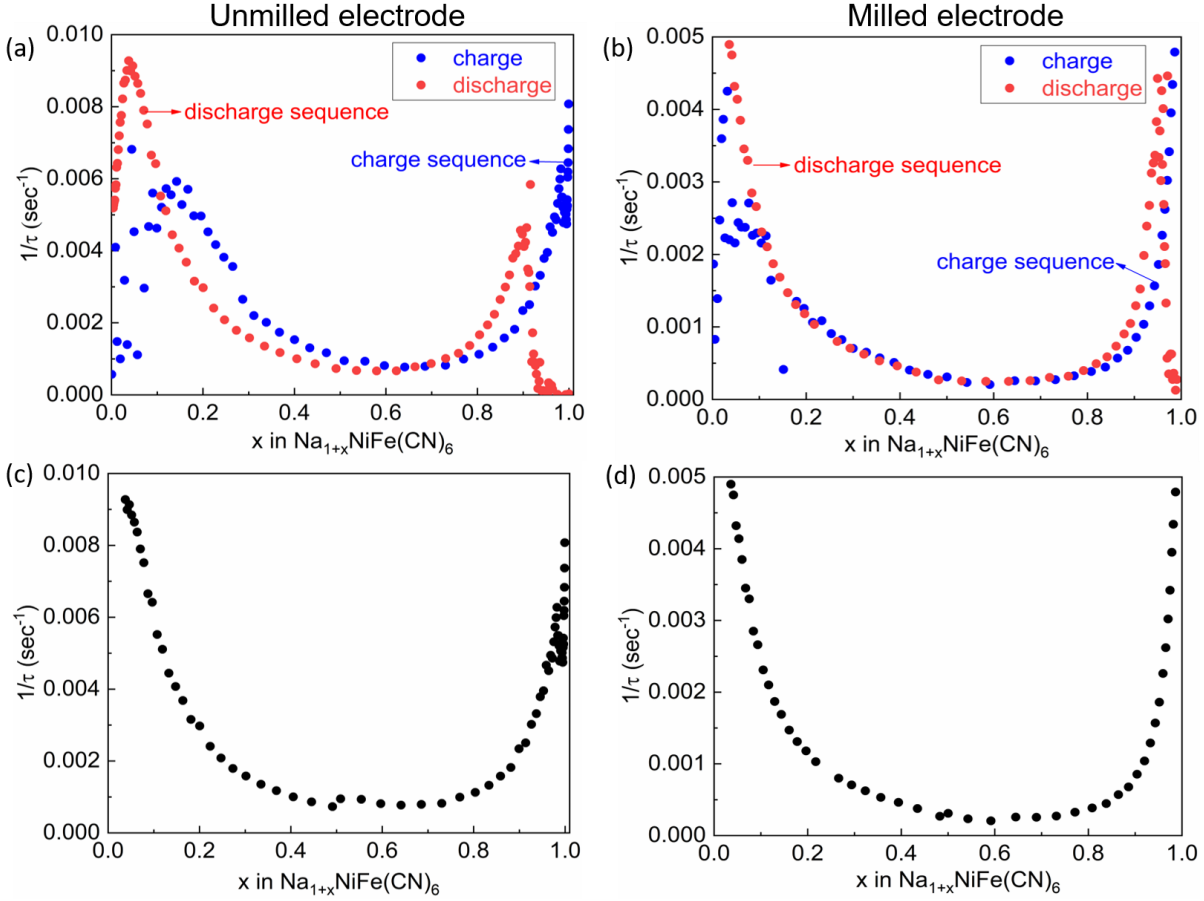


Figure B.1: Inverse diffusion time scales during charging and discharging for (a) unmilled and (b) milled electrodes respectively, and final reported $1/\tau$ for (c) unmilled and (d) milled electrodes.

The charge fraction shows an increasing trend even at long times as opposed to saturating towards unity as expected from the ideal PITT model. This unbounded increase in charge at a PITT step indicates possible side reactions (such as O_2 evolution during end of charging or carbon corrosion) that might be occurring. For both electrode types we calculated the root mean square (RMS) errors between the experimental and theoretically predicted $\Delta Q(t)/\Delta Q_{total}$ curves using the corresponding Bi and τ values fitted with short-time data for each PITT step (Figures B2(d) and B2(e)). For both electrodes, a large increase in error at the end of (dis)charging is observed, indicating that the values for $1/\tau$ obtained towards the end of the (dis)charging PITT step sequence are inconsistent with

the analytical model used to obtain the fitted parameters. This finding suggests that the associated fitted parameters are spurious. Accordingly, we neglect such values and report the final diffusion time scales corresponding to the least RMS errors, i.e., those obtained from charging for $x=0.5$ to 1.0 and from discharging for $x=0.0$ to 0.5 .

Further, during the discharge sequence for the unmilled electrode, a decreasing trend for $1/\tau$ with $x<0.03$ is observed, which is not seen in case of the milled electrode. To check whether this decrease is artificial, we examined the variation of $1/t_{50}$ with the degree of intercalation (DOI) during the discharging sequence for the unmilled electrode (Fig. B2(c)). t_{50} represents the time at which 50% of total charge is transferred during a single PITT step and hence is a surrogate for the diffusion time scale at that potential step. $1/t_{50}$ does not show a decreasing trend for $x<0.03$, while exhibiting the same trend as $1/\tau$ for all other values of x . This mismatch in the trends of $1/t_{50}$ and $1/\tau$ suggests that the diffusion time scales obtained for $x<0.03$ are erroneous experimental artefacts. Therefore, $1/\tau$ values from $x=0.03$ to $x=1$ are finally reported for the unmilled electrode (Fig. B1(c)).

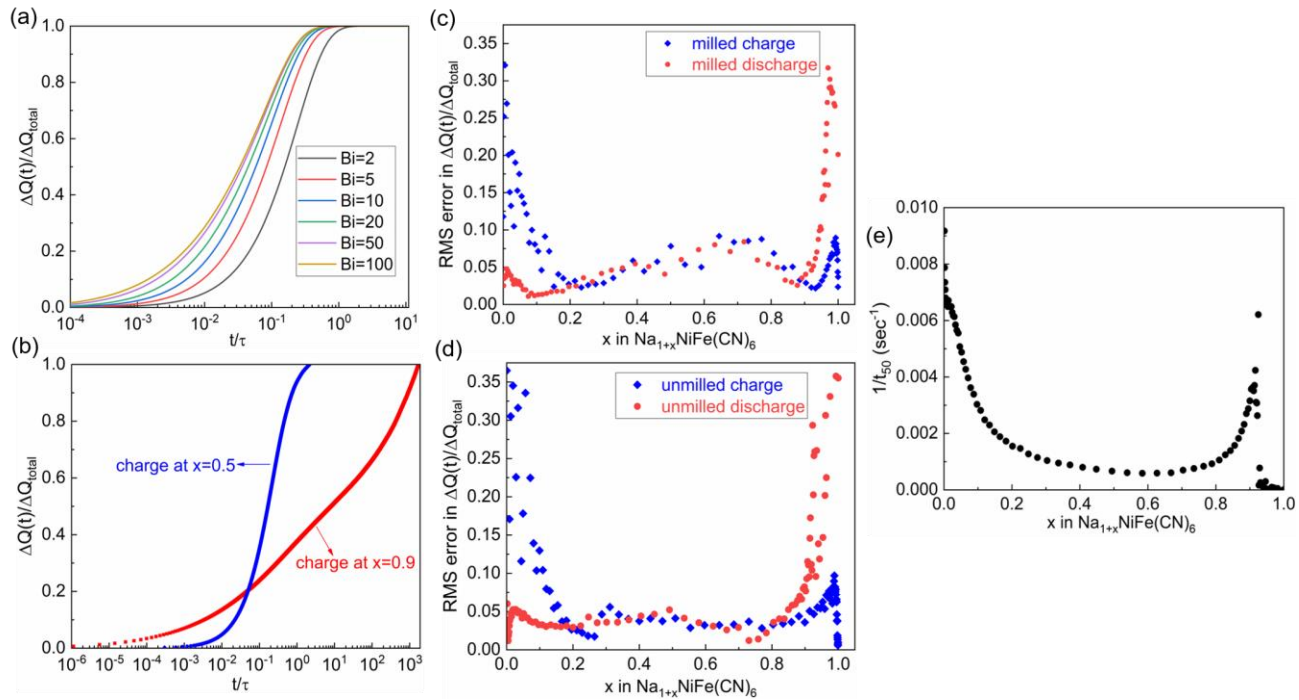


Figure B.2: (a) Theoretical response of fractional charge with time for different Biot numbers and (b) representative experimental response of fractional charge with time for the unmilled electrode during charging. RMS errors in fractional charge versus DOI during charging and discharging for (c) unmilled and (d) milled electrodes, and (e) variation of $1/t_{50}$ with DOI for the unmilled electrode.

Appendix C: NiHCFe cycling in MgCl_2 electrolyte and statistical mechanical modelling for two-site intercalation

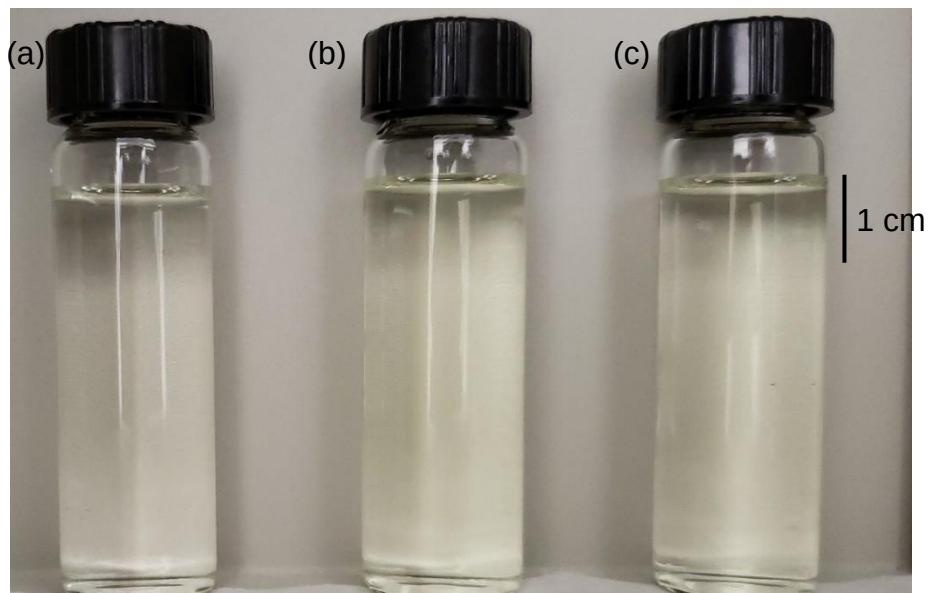


Figure C.1: $\text{MgCl}_2(\text{aq})$ electrolytes after galvanostatic cycling of (a) NiHCFe (b) MgNiHCFe and (c) $\text{Mg}_x\text{Ni}_y\text{HCFe}$

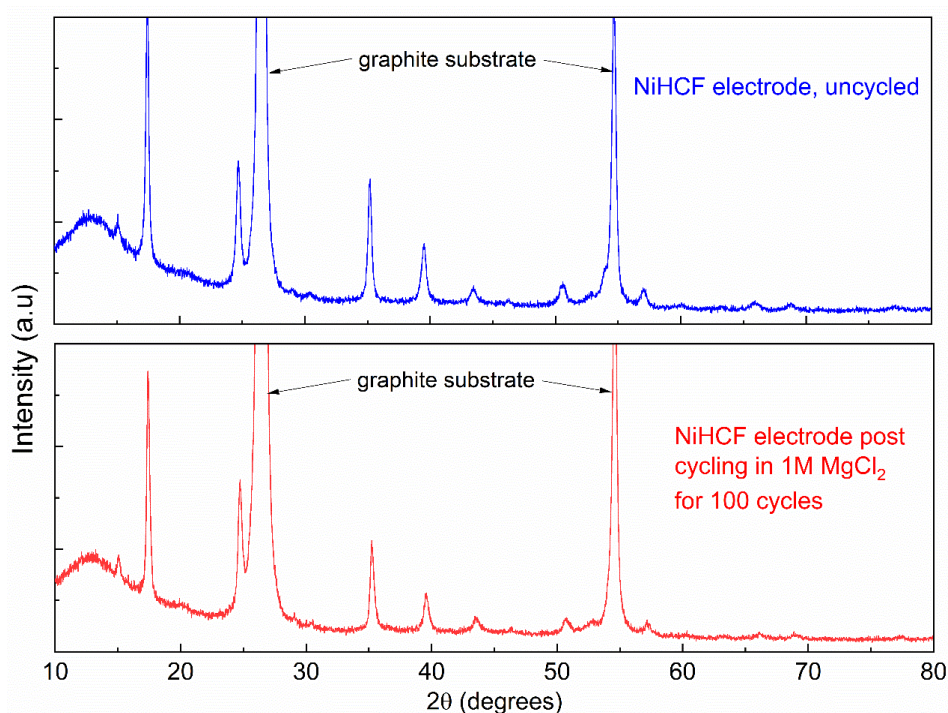


Figure C.2: X-ray diffraction of porous NiHCFe electrodes comprising of 80% active material, 10% carbon black and 10% PVDF binder, casted onto graphite substrate. No significant change in lattice parameter or crystal structure is seen even after degradation of the active material during galvanostatic cycling in $\text{MgCl}_2(\text{aq})$.

NVT ensemble analysis of a NiHCFe framework intercalated with Mg²⁺ ions to determine the fraction of Ni²⁺ ions that can be substituted by Mg²⁺

For a given supercell of size $n \times n \times n$, we have N Ni and N Mg atoms ($N = n^3/2$) in the fully intercalated configuration for NiHCFe. To calculate the fraction of Mg ions that can substitute Ni ions during intercalation, at equilibrium, we compare the pristine configuration, i.e, all Mg atoms in the interstitial sites, with swapped configurations, where 's' Ni atoms in the host sites are exchanged with 's' Mg atoms in the interstitials. The degree of swapping, 's', can vary from 1 to N . We make the following assumptions:

- i) Any Ni atom can be swapped with any Mg atom with the same probability
- ii) Energy difference between the pristine and swapped structure arising because of multiple swaps is an integral multiple of the energy difference between a singly swapped structure and the pristine structure

$$\Delta E_{s \text{ swaps}} = s \Delta E_{1 \text{ swap}}$$

Partition function for this system is given by:

$$Q = \sum_{s=0}^N \binom{N}{s}^2 \exp\left(\frac{-s\Delta E}{kT}\right)$$

Probability of a configuration with 's' swaps can be calculated as:

$$P(s) = \binom{N}{s}^2 \exp\left(\frac{-s\Delta E}{kT}\right) / Q$$

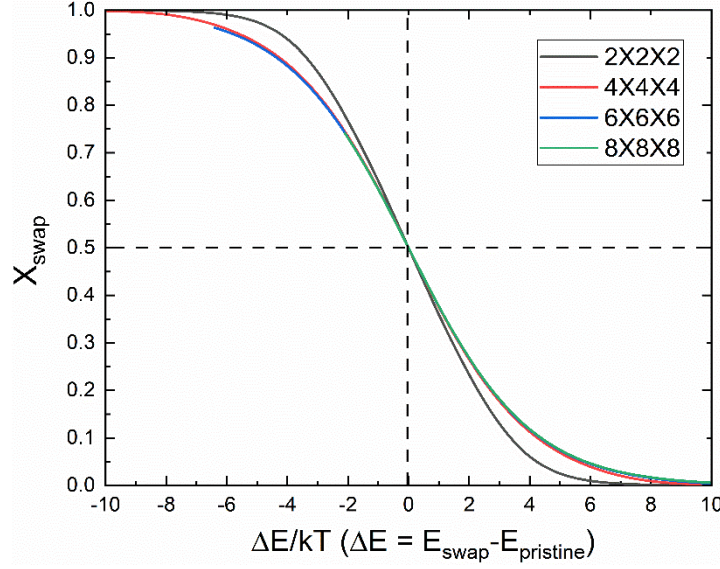


Figure C.3: Variation of the degree of swaps with energy difference between swapped and pristine structures, calculated for difference supercell sizes.

Expectation value of the number of swaps as a fraction of total number of Ni or Mg atoms

gives the substitution or swap fraction: $X_{swap} = \sum_{s=0}^N sP(s)/N$

Fig. C3 shows the degree of swapping as a function of energy difference between swapped and pristine structures, for supercell sizes starting from 2×2×2 to 8×8×8. Fig. 8 in the main manuscript uses the values from 4×4×4 supercell.

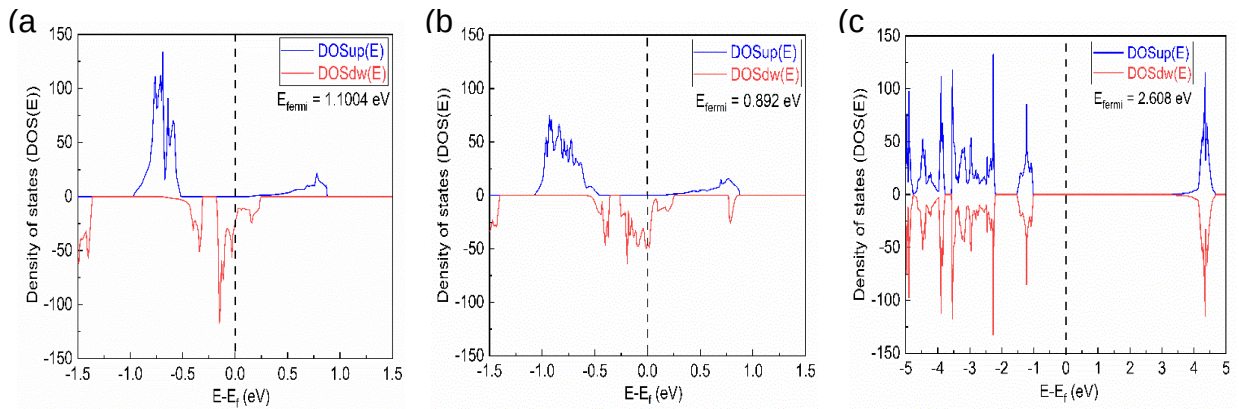


Figure C.4: Total density of states for (a) pristine configuration, (b) one-swap configuration and (c) MgHCFc.

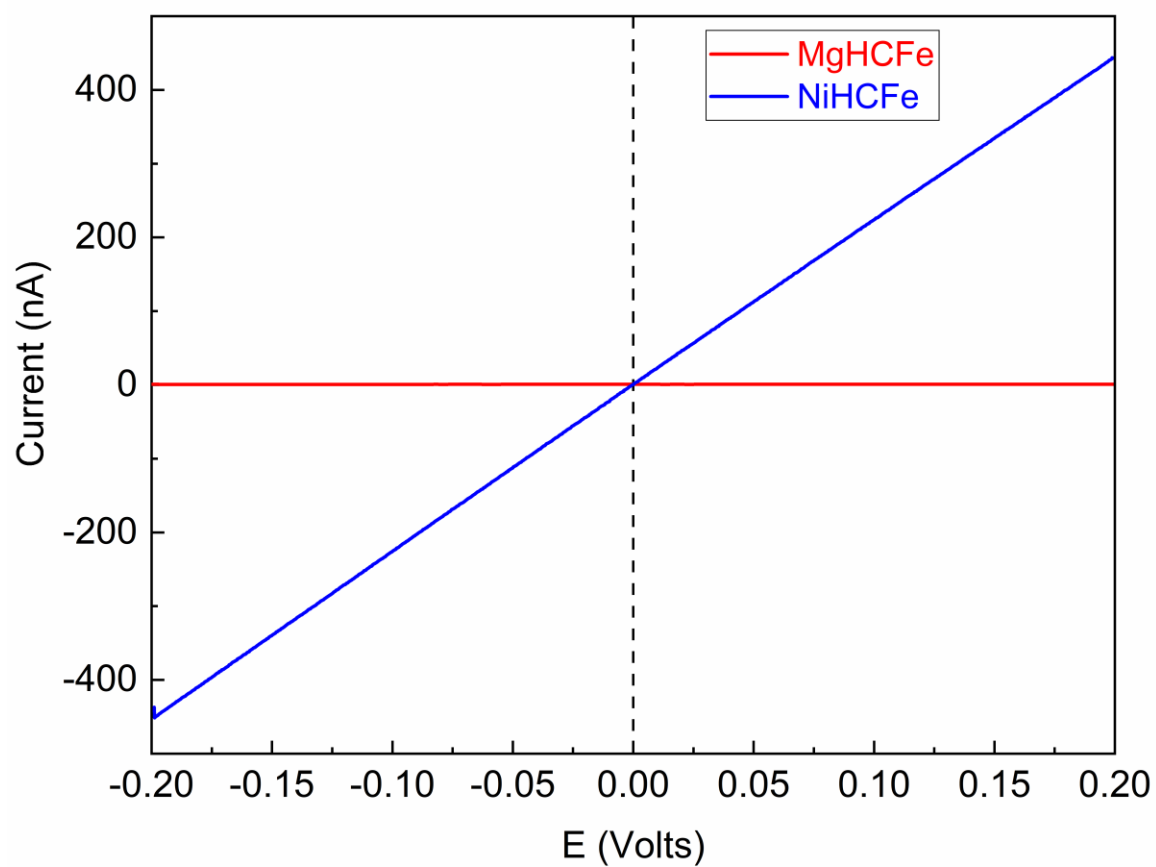


Figure C.5: Experimental current vs voltage characteristic for NiHCFE and MgHCFE powders pressed into pellets. NiHCFE shows an ohmic response whereas MgHCFE acts as an insulator, as predicted from the DOS plots in Fig. C4.

Appendix D: CO₂ dissolution equilibrium as a function of pH

Following chemical equilibria are established when CO₂(g) is dissolved in water. The corresponding equilibrium constants are obtained from literature.¹⁴⁶ All reactions are assumed to occur at a temperature of 298K.

1. $\text{CO}_2(\text{g}) \rightleftharpoons \text{CO}_2(\text{aq}); K_h = 3.4 \times 10^{-2} \text{ mol L}^{-1} \text{ atm}^{-1}$
2. $\text{CO}_2(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{H}^+; K_1 = 1.1 \times 10^{-6} \text{ mol L}^{-1}$
3. $\text{HCO}_3^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}^+; K_2 = 4.1 \times 10^{-10} \text{ mol L}^{-1}$
4. $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-; K_w = 10^{-14} \text{ mol}^2 \text{ L}^{-2}$

For initial pH >7, it is assumed that a strong base such as NaOH or KOH is added, and for pH ≤ 7, a strong acid like HCl or HNO₃ is added. Corresponding electroneutrality conditions can be written as:

- (i) pH > 7: $[\text{Na}^+] + [\text{H}^+] - [\text{HCO}_3^-] - 2[\text{CO}_3^{2-}] - [\text{OH}^-] = 0$
- (ii) pH ≤ 7: $[\text{H}^+] - [\text{Cl}^-] - [\text{HCO}_3^-] - 2[\text{CO}_3^{2-}] - [\text{OH}^-] = 0$

Using chemical equilibrium equations for 1 to 4 and the appropriate electroneutrality condition, the simultaneous set of equations was solved using MATLAB to obtain the final pH after complete dissolution of CO₂(g) and the corresponding concentrations of carbonate and bicarbonate ions.