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A rechargeable Al-metal aqueous battery using NaMnHCF as cathode: Investigating the role of coated-Al anode treatments for superior battery cycling performance

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Aqueous electrolyte, Aluminum-ion battery, Coated anode, Cycling stability, Multivalent battery

ABSTRACT: Rechargeable Al-ion aqueous batteries (AIAB) are emerging contenders for massive battery systems due to economic, abundance, environmental and safety advantages. However, the high-capacity of metallic-Al remains untapped due to native oxide barrier formation. Engineering the oxide removal by treating Al-metal with ionic liquid mixture solves this problem but the role of this treated Al (TAl) in influencing full-cell battery performance is not yet fully understood. At the same time the stability and the compatibility of the coating layer applied on Al-metal remains unexplored for long-term handling in full-cell assembly lines. Here, we explore above two aspects of TAl in the context of a full-cell AIAB. Firstly, a highly stable cathode material, NMnHCF, is demonstrated to successfully store Al-ion by reversibly transforming from monoclinic to tetragonal phase. A high energy density surpassing previous equivalent reports has been reported. Secondly, it is revealed that combinations of electrolyte-TAl pairings significantly influence the overall battery performance; wherein electrolyte conductivity influences the Al plating/stripping overpotential which in turn dictates the overall battery performance. We also document that chlorinated coatings on TAl are stable under ambient atmosphere for at least 40 hours and prevent reoxidation of the bulk aluminium metal during battery fabrication and electrochemical cycling.

1. INTRODUCTION

The risk associated with the future supply of lithium in combination with the need to produce environmentally sustainable technologies is pushing battery research and development towards non-lithium chemistries like Na, K, H, Mg, Ca, Zn, Al.¹⁻¹⁵ Among all, using Al-metal as an anode is particularly advantageous because of its highest volumetric capacity (~8000 mAh cm⁻³) and high abundance in the earth's crust; thus opening up the possibilities for sustainable and affordable batteries for everyone.¹⁶⁻¹⁸ Various rechargeable Al-ion battery (AIB) systems using either non-aqueous or aqueous electrolyte have been demonstrated recently.^{4, 17, 19-20} Whereas conventionally AIB have been assembled with non-aqueous electrolytes, aqueous electrolytes provide added advantages in terms of intrinsic safety because of non-flammability and non-volatility of water. This makes aluminum-ion aqueous battery (AIAB) an ideal candidate for large scale applications such a grid-scale energy storage where safety and economic sustainability are more important considerations.

However, AIAB research is still in a nascent stage, with very few theoretical works though none including multiscale

simulations,²¹⁻²² and existing challenges at both cathode and anode front. Cathodes suffer from various problems such as low voltage²³⁻²⁸, poor capacity²⁹⁻³⁵, rapid cycling decay³⁶⁻³⁹, and predominant capacitive reaction⁴⁰⁻⁴¹. Though few reports including PBA,⁴² graphite⁴³, Bi₂O₃⁴⁴ and VOPO₄⁴⁵ are promising, these studies do not use Al-metal as an anode, thus lack in providing a more realistic scenario of overall battery performance. A full cell study is critically important because it is the usage of Al-metal as anode which potentially makes AIAB cheaper than other metal battery systems. Only until very recently (December 2018), all the research reports for AIAB had been deployed for 3 electrode setup or used non-Al anode in two-electrode setups.¹⁷⁻¹⁸ Previous attempts to use Al-metal anodes had failed due to ionically-insulating native oxide layer that readily forms over Al, making it impractical to plate/strip Al without significant electrolyte decomposition. A breakthrough in this direction came from Prof. Archer et al. wherein they chemically treated Al foil surface in an inert atmosphere using a mixture of AlCl₃ and ionic liquid. This formed an artificial conductive layer on the surface and changed the surface chemistry by preventing native oxide formation, thus enabling Al plating/stripping with significantly reduced overpotential.⁴⁶

Figure 1. (a) Experimental XRD pattern of synthesized NMHCF powder with Bragg lines of matched phase, (b) Thermogravimetric analysis (TGA) curve and (c) Crystal structure of the synthesized NMHCF powder.

Following Archer et al.'s work, studies making use of similar approach have been reported.^{36, 47-49} Currently, there is no existing study, other than the first report on TAl,⁴⁶ that focuses on the role of treated Al (TAl) anode, if any, in determining the overall battery performance. At the same time, there is no existing knowledge about the stability of this artificial coating when exposed to ambient environment or its compatibility in a functioning AIAB cell. Both these aspects are critically important in furthering our confidence to use TAl as an anode in AIAB.

Here we explore these two aspects of TAl anode in the context of a full-cell AIAB: 1) Firstly, a novel host material, $\text{Na}_{1.68}\text{Mn}[\text{Fe}(\text{CN})_6] \cdot 1.7\text{H}_2\text{O}$ (NMHCF), is tested alongside TAl and stable cycling performance is obtained by optimizing the electrolyte concentration. We report a high energy density that surpasses the performance of its equivalent HCF-Al full cell reports in AIAB and elucidate the concomitant mechanism of Al-ion intake^{34, 50}. 2) Secondly, TAl is identified to actively influence battery performance. When using TAl as anode, Al plating/stripping overpotential becomes a key factor in obtaining improved battery cycling life. The effectivity of TAl coating is further evidenced by our system entering a diffusion polarization regime wherein it is the electrolyte conductivity that limits charge/discharge reversibility. 3) Thirdly, the stability of the coating on the TAl anode is studied both under atmosphere aging and postmortem from working battery cells. Overall, we present a comprehensive perspective of a full cell AIAB by reporting a novel high-performance cathode and adding important knowledge towards the usage of TAl anode in AIAB field.

2. RESULTS AND DISCUSSION

2.1 CHARACTERIZATION OF NMHCF POWDER

A Prussian blue analogue (PBA) was chosen for this study as they are high voltage materials and have been reported to show good cycling stability in aqueous electrolytes.¹⁷ Figure 1a shows the diffractogram of the synthesized material which matches well with the monoclinic phase - $\text{Na}_{1.68}\text{Mn}[\text{Fe}(\text{CN})_6] \cdot x\text{H}_2\text{O}$ (PDF 04-022-3444).⁵¹ A Pawley fitting with P21/n space-group rendered lattice parameters as $a = 10.5807(6) \text{ \AA}$, $b = 7.513(1) \text{ \AA}$, $c = 7.3187(9) \text{ \AA}$, $\alpha = \gamma = 90^\circ$, $\beta = 92.16(1)^\circ$. Thermogravimetric analysis (Figure 1b) was used to determine the percentage of water in the synthesized material. The weight loss occurred firstly as desorption of water from the

material surface, followed by a significant weight loss of 9.25% which could be assigned to the elimination of interstitial water.⁵¹ Second step water loss corresponds to 1.73 water molecules per $\text{Na}_{1.68}\text{Mn}[\text{Fe}(\text{CN})_6]$ unit. The structure of NMHCF (Figure 1c) is a 3D open framework formed with C-N anions bridging MnN_6 and FeC_6 octahedron, leading to the formation of large interstitial voids (which is currently occupied by Na ions). Such large voids ($\sim 4.6 \text{ \AA}$) are apt for accommodating high charge density ions like Al^{3+} or its hydrated complexes which have a comparatively large diameter ($\sim 3.8 \text{ \AA}$).^{31, 52} This makes PBA's crystal structure ideal for studying multivalent battery chemistries.

2.2 ELECTROCHEMICAL PERFORMANCE

Cyclic voltammetry (CV) was used to study the activity of NMHCF towards the uptake of Al-ion (Figure 2a). Prominently, a broad pair of peaks was observed with anodic peak and cathodic peak at 1.75 V and 1.1 V, respectively, averaging to a voltage of 1.42 V vs. Al^{3+}/Al . The broadened nature of peaks indicates a complex insertion mechanism as also observed previously for HCFs^{24, 29, 31}, including possibly a de-solvation of hydrated Al-ion complex at cathode-electrolyte interphase.⁵³ The galvanostatic charge-discharge (GCD) profile (Figure 2b) consisted of a single flat plateau, both for charge and discharge, consistent with the singular pair of main peaks in the CV study. Upon subsequent cycling, though the plateau profiles remained consistent, they grew apart indicating an increase in the charge/discharge overpotential. **Notably, overpotential keeps on increasing even after the 10th cycle (Figure S1b). Plating/stripping of symmetric TAl cell (Figure S1c) suggests that the initial ($\sim$ first 10 cycles) increase in the overpotential is majorly contributed by the cathode side as plating/stripping overpotential almost remained constant in the first 10 cycles. This cathode overpotential may result in a rapid decay of capacity in first few cycles as has also been observed in other Al aqueous work with HCF cathode, when not using Al anode^{32, 42} and also when using Al as anode³⁴.** As a control reaction, the activity of NMHCF was also tested in a 2 m solution of HCl (Figure S1d). No cathodic peak was observed, essentially indicating negligible co-insertion of H^+ during discharge.³⁷

Further, the cycling behaviour of the cathode was studied in varying concentrations (0.1, 0.7, 2, 2.5, 3, 5 m) of $\text{Al}(\text{OTf})_3$ electrolyte at a constant current rate (Figure 2c). Cycling performance improved with the increase in electrolyte

concentration until 2 m and then decreased for more concentrated electrolytes. Interestingly, this observation is contrasting to the conventional knowledge that more concentrated electrolytes are better for good cycling stability owing to their wider

thermodynamic stability window and suppressed side reactions with cathodes.⁴² We investigate and discuss this anomalous observation further in section 2.4.

Figure 2. Electrochemical activity of NMHCF in a full cell with TAl as anode: (a) Cyclic voltammograms in 2 m Al(OTF)₃ between 0.6 V and 1.9 V vs. Al³⁺/Al, at a scan rate of 0.1 mV s⁻¹, (b) Galvanostatic charge/discharge profile in 2 m Al(OTF)₃ at a current rate of 30 mA g⁻¹, (c) Cycling stability study for various concentrations of Al(OTF)₃ aqueous electrolyte at the current rate of 100 mA g⁻¹, (d) Cycling stability study at various current rates in 2 m Al(OTF)₃ aqueous electrolyte, (e) Extended cycling performance and corresponding coulombic efficiency in 2 m Al(OTF)₃ aqueous electrolyte at 30 mA g⁻¹.

Cycling performance also improved significantly upon reducing current rates. In a 2 m electrolytic solution, the stable capacity improved by ~10 folds as the current rate was decreased from 200 mA g⁻¹ to 10 mA g⁻¹. **We ascribe the improved capacity as a result of better insertion kinetics at slow-cycling rate and better cycling stability as a result of reduced anodic over-potential at slow-cycling rates (Figure S1e).** Having optimized the electrolyte concentration and observed better battery cycling performance at the reduced current rate, the full cell was studied for extended capacity retention at 30 mA g⁻¹ in a 2 m electrolyte solution. A stable cycling life with a high energy density starting from 130 Wh kg⁻¹ was observed, which eventually decreased to 60 Wh kg⁻¹ over 275 cycles. This performance is significantly better than the only two HCF-Al full cell reports in AIAB field, reporting energy densities of 15 Wh kg⁻¹ and 40 Wh kg⁻¹.^{34, 50}

2.3 REACTION MECHANISM IN NMHCF

The reaction mechanism in NMHCF was studied using ex-situ XPS, XRD and Raman spectroscopy. Ex-situ XPS was used to detect the presence of Na and Al in the electrodes and to study the oxidation state changes on the transition metal centres, Fe and Mn. Na 1s region of the XPS spectra (Figure S2a) shows a considerable presence of Na in the pristine cathode, as expected.

Upon charge, this amount decreases significantly, only to increase slightly on subsequent discharging. This essentially indicates that most of the Na was removed in the first charging step and Na does not contribute significantly to the discharge capacity. Al 2p region of XPS spectra (Figure S2b) showed the abundant presence of Al in the discharged cathode, which was lacking in the pristine cathode, essentially indicating insertion of Al-ion during discharge. **Notably, Al2p binding energy in the discharged cathode was ~ 3 eV lower than in Al(OTF)₃ salt,⁴² implying a changed chemical environment for Al-ion which may have resulted because of insertion of Al-ion in the host material and finally leading to the formation of a stable Al-inserted compound.**

Changing oxidation states on transition metal centres also support the reversible insertion mechanism of Al-ion in NMHCF. Fe (Figure 3a) which was present as +2 oxidation state in the pristine electrode (Fe 2p_{3/2} – 707.97 eV; Fe 2p_{1/2} – 720.85 eV),⁵⁴⁻⁵⁵ oxidized to mixed oxidation states +2 and +3 upon charging (Fe 2p_{3/2} – 707.82 eV and 708.81 eV; Fe 2p_{1/2} – 720.78 eV and 722.82 eV)³⁴. Upon subsequent discharge, the oxidation state of Fe was restored to the original value of +2 (Fe 2p_{3/2} – 707.93 eV; Fe 2p_{1/2} – 720.80 eV). Mn (Figure 3b) showed similar changes in oxidation state upon cycling. In the pristine electrode, Mn was present in mixed oxidation states of +2 and +3 with Mn²⁺/Mn³⁺ ratio of ~ 3:2 (Mn 2p_{3/2} – 640.69 eV and

641.85 eV; Mn 2p_{1/2} - 652.75 eV and 654.30 eV).⁴⁹ Upon charging Mn²⁺/Mn³⁺ ratio changed to ~1:1, indicating oxidation of Mn. Further, upon subsequent discharge, Mn²⁺/Mn³⁺ ratio was restored to the original value of 3:2. Overall, a reversible change of oxidation state on both the transition metal centres

indicates two things: 1) successful reversible insertion/extraction of Al-ion in the host structure and 2) both the transition metals accommodate for charge variations happening in the host material during cycling.

Figure 3. (a) Fe 2p and (b) Mn 2p region of XPS spectra for pristine, charged and discharged NMHCF cathodes. (c) Ex-situ X-ray diffractograms of the NMHCF cathode collected in pristine, and at the end of 1st and 4th cycle in charged (1 C and 4 C) and discharged (1 D and 4 D) states. (d) Schematic illustration of structural evolution in NMHCF upon cycling.

Ex-situ XRD (Figure 3c) shows the reversible structural transformation in NMHCF from monoclinic to tetragonal phase upon cycling. X-ray diffractograms were collected for cathodes at the end of 1st and 4th cycle in charged (1 C and 4 C) and discharged (1 D and 4 D) states. Firstly, the pristine cathode was matched, and Pawley-fitted with a monoclinic, P2₁/n, space-group. Upon charging (1 C and 4 C), few peaks started to disappear while the prominent peaks of pristine cathodes remained as it is, indicating a transformation of NMHCF to a more symmetrical crystal structure. In previously reported Na and K ion battery systems using MnHCF as the cathode, HCFs have been reported to transform into tetragonal crystal structures upon charging.^{51, 55-56} Hence diffractograms for the charged cathodes were Pawley-fitted with a tetragonal space group, $\overline{1}4m2m$. Upon subsequent discharging, the original peaks characteristic of the monoclinic phase reappeared. Figure S3 shows the resultant lattice parameters from the Pawley fitting of diffractograms in Fig. 3c. Firstly, it is observed that the variation of lattice parameters is highly reversible comparing the 1st and 4th cycles. Upon charging, lattice parameter *c* expands and becomes equal to *b* (also causing an increase in lattice volume), and the angle β changes to 90°. Upon subsequent discharge, *c* contracts by ~0.14 Å (lattice volume also decreases) and β changes to ~92°. The lattice parameter for the discharged cathode is the same as that of pristine cathode indicating reversible structural transformation. Such reversible monoclinic to tetragonal transformation is common for HCF and just like previously reported Na-ion and K-ion studies, we observe same for Al-ion insertion as well.^{51, 55-56} Notably, two new shoulder peaks (marked with

a star in diffractogram of 4 C) appeared in the discharged cathode diffractogram. Though quantitatively negligible, these peaks may belong to a cubic phase of HCF,⁵⁷ formed midway during charging/discharging as also reported previously.^{51, 55-56}

Ex-situ Raman study indicates local structural reversibility upon cycling. The pristine electrode (Figure S4) showed the presence of two main peaks at 2026 cm⁻¹ and 2105 cm⁻¹ which can be attributed to the mixture of Fe^{II}-CN-Mn^{II} and Fe^{II}-CN-Mn^{III}.⁵⁸⁻⁵⁹ Upon charging (1 C and 4 C) these peaks disappear almost completely and reappear on subsequent discharging (1 D and 4 D). This indicates high reversibility in the local structure of NMHCF.

Based on inferences from all the ex-situ studies, the proposed mechanism of insertion/extraction along with host crystal structure change is presented in Figure 3d; showing removal of Na in the first charge step followed by reversible insertion/extraction of Al-ion in subsequent cycling which results in a reversible phase transformation from monoclinic to tetragonal phase.

2.4 ROLE OF TREATED Al-ANODE

The idea of using highly concentrated electrolyte (water-in-salt) in aqueous battery systems has been widely held as such electrolyte provides a wider electrochemical stability window and suppresses the side reactions of the cathode, enabling better cycling life performance.^{36, 60} Even for HCF cathode based

AIAB, the water-in-salt concept had been implemented previously by using 5 m $\text{Al}(\text{OTF})_3$, either in 3 electrode setup⁴² or in HCF-Al full cell.³⁴ But our observation (in section 2.2, as illustrated in Figure 2c) is counter-intuitive to the water-in salt concept as optimal full cell performance was obtained in 2 m

electrolyte and not for higher concentrations like 3 m or 5 m. In this section, we try to answer this discrepancy and relate it to the usage of TAl which has only recently penetrated AIAB research

Figure 4. (a) Conductivity vs. $\text{Al}(\text{OTF})_3$ electrolyte concentration plot (in grey); and NMHCF-TAl cell charge /discharge overpotential obtained for various concentrations of $\text{Al}(\text{OTF})_3$ electrolyte including 0.1 m, 1 m, 0.7 m, 2 m, 2.5 m, 3 m, and 5 m, (shown for 1st, 5th and 20th cycle). (b) Cycling stability study of FeVO_4 -TAl cell for various concentrations of $\text{Al}(\text{OTF})_3$ aqueous electrolyte (0.1 m, 1 m, 2 m, 5 m) at the current rate of 150 mA g^{-1} . (c) Stripping/plating testing in symmetric TAl cell for various concentrations of $\text{Al}(\text{OTF})_3$ aqueous electrolyte (0.1 m, 1 m, 2 m, 5 m); Negative and positive current density of 0.2 mA cm^{-2} was applied for 1 hour each in an alternating sequence.

and needs more investigation especially in terms of its effects on full cell performance.

Firstly, we tried correlating electrolyte's transport property to the optimal cycling performance observed for 2 m $\text{Al}(\text{OTF})_3$ by studying overpotential trends in NMHCF-TAl full cells. A clear idea of overpotential evolution during runtime can be obtained from full cell charge/discharge profiles plotted for various electrolyte concentrations (Figure S5). It can be observed that the charge/discharge voltage plateau difference in 2 m electrolyte cell is less as compared to cells with other concentration of electrolytes and this difference remains low even after repeated cycling (5th and 20th cycle). This overpotential variation is summarized in Figure 4a for the 1st, 5th and 20th cycles. Plotting overpotential against electrolyte concentration forms an inverted bell curve. Interestingly, electrolyte conductivities measured over 0.1 m to 5 m concentration form a bell curve and its maxima almost coincided with the overpotential-concentration minima. This hints that electrolyte's conductivity may have a role in determining the battery overpotential and eventually the

battery cycling performance. But previous studies on HCF for AIABs, done in 3-electrode configurations, report that the best cycling performances are achieved in the most concentrated $\text{Al}(\text{OTF})_3$ electrolytes, although they do not exhibit maximum conductivity.⁴² This inconsistency seems to hint that electrolyte optimization alone is an insufficient approach, as other components may have yet unidentified synergistic or antagonistic effects with particular electrolyte compositions.

It is very well possible that "electrolyte + cathode" combination can be responsible for influencing battery cycling life. Thus, as a controlled study, we change the cathode and study the cycling performance with varying concentration of electrolyte. For this purpose, FeVO_4 was chosen as it is a conversion type material which shows a completely different mechanism of Al-ion uptake than NMHCF, thus inferences could be made independent of the Al-ion insertion mechanism.³⁹ Even for FeVO_4 , the best cycling life was obtained in 2 m electrolyte and not in a more concentrated electrolyte of 5 m (Figure 4b). Like NMHCF, the least cell overpotential was observed when 2 m

electrolyte was used (Figure S6). Since changing the cathode did not disrupt the trend of obtaining best cycle life for a relatively less concentrated electrolyte, it is safe to infer that different “electrolyte + cathode” pairings would result in analogous overall cell performances, and that the cathode immersion in the electrolyte was not limiting the capacity retention.

As a next possibility the “electrolyte + anode” combination could have been responsible for influencing battery cycling life. Therefore, stripping/plating tests were done in a symmetric TAl-TAl cell to study the overpotential development for various electrolyte concentrations (Figure 4c). Interestingly, the least Al plating/stripping overpotential was observed for the case of 2 m electrolyte while higher overpotentials were observed in less (0.1 m and 1 m) and higher (5 m) concentrations. This has the same trend as cycling life variation with electrolyte concentration observed for both NMHCF and FeVO_4 host material. Thus, it can be safely inferred that here, the “electrolyte + anode” pairing is responsible for influencing battery cycling performance.

We speculate that very highly concentrated electrolyte due to their reduced conductivity might hinder the ionic transport at electrolyte-TAl surface interface causing increased overpotential, eventually resulting in bad cycling performance. Here we highlight again that when varying electrolyte concentration, while not using Al as an anode, the cathode cycling life is likely to improve with an increase in concentration. For example, Suo et al. in a three-electrode setup without Al-metal as anode observed the most stable cycling life for HCF Al-ion host material in a 5 m $\text{Al}(\text{OTF})_3$ and not in less concentrated $\text{Al}(\text{OTF})_3$.⁴²

At this stage, it becomes clear that using TAl as an anode in a full cell AIAB has significant implications. The electrolyte conductivity strongly influences the Al stripping/plating overpotential, which in turn dictates the overall battery cycling performance. Thus an “electrolyte + anode” combination becomes the key factor in influencing cycling life when fabricating a full cell using TAl. At the same time concepts such as water-in-salt, which may work in 3 electrode setups, do not necessarily translate to similar benefits when transitioning to TAl anodes.

Figure 5. Al 2p region of XPS spectra for first three layers of (a) Al foil, (b) TAl foil, (c) TAl exposed to air for 40 hours, (d) TAl foil cycled in a symmetric cell with 2m Al(OTF)₃ as the electrolyte. XPS data was first collected from the surface, followed by two rounds of etching (60 s Ar⁺ sputtering) and data collection.

2.5 STABILITY/COMPATIBILITY STUDY OF THE TREATED-AL ANODE

Indeed, the introduction of usage of TAl as anode has effected a shift in the AIAB field with studies conventionally done in 3 electrode setups shifting towards a more realistic scenario of 2 electrode setups. Clearly, majority of AIAB reports post⁴⁶ tried to use Al foil as anode, in original form^{34, 40, 44, 47, 49, 61} or in a modified form^{36, 48, 62}. Unfortunately, in all these studies either cathode or electrolyte remained the focus of the study and no detailed work focused on the TAl coating stability or TAl compatibility with aqueous electrolytes exists. Documenting stability/compatibility of TAl is important because: 1) battery fabrication is done in an ambient environment where TAl is exposed to O₂ and moisture. This may change its surface chemistry, eventually affecting the battery performance and 2) we have no existing knowledge on how the artificially formed protective coating on Al behaves when inside a working cell.

In this section we try to document stability/compatibility of TAl by studying the surface layers of pristine Al foil (Al), TAl foil (TAl), TAl foil which has been exposed to air (TAl_{air}) and TAl foil cycled in a cell (TAl_{cycled}). Essentially, by identifying the chemical species on the surface and just beneath it, we try to make sense of stability/compatibility of the coating layer. Figure 5 shows the XPS spectra for the respective foils, wherein the surface of the foil has been characterized followed by two rounds of etching & characterization. Table S1, S2 and S3 show the binding energy values for all the chemical species discussed in this section.

For pristine Al foil surface, the Al 2p region of the XPS spectra showed the presence of two distinguishable peaks (Figure 5a). These could be deconvoluted into three peaks representing metal Al⁶³⁻⁶⁴, Al₂O₃⁶⁵⁻⁶⁷ and the native oxide layer on Al (AlO_x)⁶⁵⁻⁶⁷. Upon 1st etch, the amount of both the oxides decreased significantly as indicated by their low intensity deconvoluted peaks. Further, the XPS envelope remained the same after the 2nd etch. Upon etching, the O1s region of XPS spectra shifted to higher binding energy and its intensity dropped significantly (Figure S7). This also supports the facts that most of the metal oxide gets removed upon etching and the remnant oxygen is likely from organics and not metal oxide. Notably, in all the three layers sampled, there is no hydroxide present as the O1s spectra binding energy remained at a lower value than known for hydroxides (534 eV).⁶⁸

Upon treating the Al-foil, the Al surface layer was appreciably modified, giving rise to a conspicuously different spectra (Figure 5b) as compared to Figure 5a. The TAl surface majorly showed the presence of AlCl₃ species⁶⁹, also corroborated by the presence of Cl (Figure S8), which was originally present in the coating solution applied onto Al foil. Interestingly, even

after two rounds of etching, the surface chemistry did not change, indicating that the coating layer was thick.

Further, TAl foil was exposed to the ambient air for 40 hours (TAl_{air}) and then characterized. As can be seen from the spectra (Figure 5c), the surface chemistry did not change significantly. The surface layer still had the abundant presence of AlCl₃ with a very small amount of Al hydroxide (deconvoluted peak of O1s spectra at 534.44 eV also corroborates hydroxide presence (Figure S9))^{68, 70-71}. Upon etching, the exposed surface still indicated an overwhelming presence of AlCl₃, with a gradual removal of the hydroxide layer and a small presence of the native Al oxide layer. We would like to highlight that in our battery fabrication process, TAl needed to be exposed only for a few minutes in an ambient environment before being assembled in a coin cell. Hence the coating layer is sufficiently good for the fabrication process.

Upon cycling TAl (in symmetric TAl cell for two cycles), major changes are seen in the surface chemistry of TAl (Figure 5d). Firstly, only one peak is seen for Al at 76.50 eV. At the same time, new peaks in the C1s region of the XPS spectrum emerges (Figure S10a), corresponding to CF₃, COOH, C=N, C-N and C-S functional groups. CF₃ and C-S are likely from Al(OTF)₃ electrolyte, whereas C=N and C-N from the ionic liquid used in coating and COOH may have formed in-situ. O1s is also shifted to higher energy with two peaks at 533.64 eV and 534.21 eV (Figure S10b). The major peak at 533.64 eV corresponds to the oxygen in SO₃⁻,⁷² which may have come from the Al(OTF)₃ electrolyte. At the same time, F is also detected (Figure S10c) and corresponds to organic flouride⁷³. Hence Al detected here is ascribed to AlCl_xF_y⁶⁹. Overall, the presence of organic functional groups and AlCl_xF_y indicates the formation of in-situ solid electrolyte interphase (SEI). Upon etching, four components are seen in the Al2p region: Metal Al, Al₂O₃, Al hydroxide and Al(OTF)₃. XPS of TAl soaked in a cell for 12hrs (Figure S11) show that this Al hydroxide and a small amount of Al₂O₃ may have formed because of coating layer reacting with electrolyte and can prove detrimental to cycling performance. Here we would also like to highlight that, even though a hydroxide layer has formed over Al, it is not as thick as the oxide layer observed on the surface of as received Al-foil (Figure 5a). Upon further cycling, no major changes in the surface chemistry is seen (Figure S12). AlCl₃ was detected randomly but in small quantity (Figure S13) on the surface of TAl_{cycled} but at the same time some organic components of protective coating remained (Figure S12 b). This indicates that protective coating used in treating of Al may have partial broken during cycling/in rest and Cl may have partially dissolved in the electrolyte. Hence, it is likely that a combination of partially broken protective coating and in-situ formed SEI layer exists through the cycling and may be responsible to avoid severe oxidation of Al foil.

Overall, we infer that the protective coating is stable in the ambient environment and helps avoid oxide formation in the

ambient environment when Al is being transferred from the inert atmosphere and assembled into a cell. But this coating is not very compatible in a working aqueous cell and breaks partially during cycling. Rather it is the “partially broken protective coating + SEI” layer that helps in avoiding severe oxidation of Al when cell is operation. Nevertheless, the protective coating did break inside while cycling. Therefore, there is still a need to find a new kind of coating which is more stable in-situ cycling.

3. CONCLUSION

In this study we try to provide a comprehensive picture of a full cell AIAB, especially considering the implications of using a chemically treated Al (TAI) as anode.

Firstly, we report a highly stable PBA analogue, NaMnHCF, that can readily store Al-ion by transforming from monoclinic to tetragonal phase. Such a transition is observed to be highly reversible during repeated charge/discharge and Al-ion insertion in the host material is mainly attributed to the large interstitial voids and accommodation of charge variation by multiple transition centers in host, namely, Fe and Mn. We report a high energy density of 130 Wh kg⁻¹ which decays to 60 Wh kg⁻¹ over 275 cycles. This performance is above par full-cell HCF reports in AIAB field and the improvement in performance is attributed to the usage of right combination of cathode + electrolyte + anode for the fabrication of AIAB cell.

Secondly, we highlight the crucial implications of using TAI as anode in an AIAB system. It is revealed that when using TAI, the overall cycling performance of the cell is a strongly influenced by “electrolyte + TAI” combinations. We observed that electrolyte’s conductivity affects the Al stripping/plating overpotential which in turn dictates the overall battery cycling life. Hence, when using TAI, it becomes important to consider the factors that can influence Al stripping/plating overpotential. At the same time, conventional concepts like water-in-salt needs to be re-evaluated as they may not translate to similar benefits when transitioning to TAI anodes. We also document that: 1) the coating layer on TAI is sufficiently stable in ambient conditions and helps hinder the formation of oxide layer on Al. 2) the coating layer may partially break during cycling, but an in-situ SEI layer formation takes place which helps in avoiding severe oxidation of Al anode during cycling.

This study adds strategies towards the fabrication of stable AIAB and furthers our confidence towards the usage of TAI in the AIAB field.

ASSOCIATED CONTENT

Supporting Information

Synthesis procedure of NMHCF, characterization methods, electrochemical measurement methods, Raman data, GCD profile related to overpotential evolution, and supporting XPS data have been provided in Supporting information.

The Supporting Information is available free of charge on the ACS Publications website.

(PDF)

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Author Contributions

All authors have given approval to the final version of the manuscript.

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