

## Supporting information for

### **Alkaline-based aqueous sodium-ion batteries for large-scale energy storage**

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## Supplementary Discussion

### Text S1. Function of carbon in Ni/C coating.

The binder was Nafion-Na which forms a dense coating on the surface of the cathode. With low ionic conductivity, it increases interfacial resistance and compromises rate performance. Adding carbon matrix improves the porosity of the polymer and conductivity of the coating, ameliorating the detrimental effect of the coating on rate performance. As shown in **Supplementary Figs. 13a-b**, following the introduction of the carbon matrix, the resistance of the coating with a thickness of 25  $\mu\text{m}$ , was reduced from *ca.* 150 to  $< 10\ \Omega$ , evidencing that carbon addition reduces the interfacial resistance of the coating. However, because of the absence of Ni, the carbon coating itself cannot induce a  $\text{H}_3\text{O}^+$ -rich local environment to suppress OER and cathode dissolution. Therefore, batteries with pure carbon coating exhibit significant over-charging caused by water decomposition (**Supplementary Fig. 13c**) and poor cycling performance induced by cathode deterioration (**Supplementary Fig. 13d**).

### Text S2. The barrier effect of coating on $\text{OH}^-$ migration.

Experiments were conducted to establish the barrier effect of this coating material on  $\text{OH}^-$  migration. An H-cell configuration, illustrated in **Supplementary Fig. 16**, was used. An alkaline electrolyte with a pH of 12.3 was introduced into the left-side of the H-cell, whilst a neutral electrolyte with a pH of 6.5 was added to the right-side, in which the uncoated cellulose, Nafion-Na coated cellulose, and Ni/C coated cellulose were used as separators, respectively. During the resting phase,  $\text{OH}^-$  ions in the left-side of the H-cell migrate to the right-side, resulting in an increase in pH in the right-side. To quantify this effect, a pH meter was used to determine the rate of pH increase in the right-side. As seen in **Supplementary Fig. 17**, in comparison with the uncoated cellulose, the Nafion-Na coated cellulose exhibits a suppression of  $\text{OH}^-$  ion migration, and the Ni/C boosts this effect.

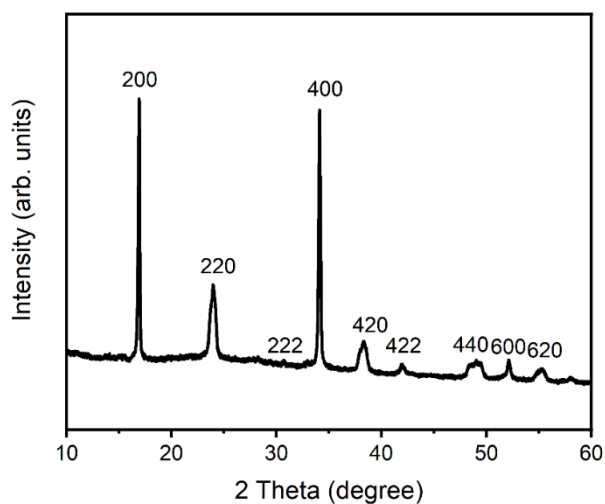
### Text S3. Transformation of Ni in coating and contribution to H<sub>3</sub>O<sup>+</sup>-rich local environment.

Generation of H<sub>3</sub>O<sup>+</sup> is predicated on two transformation steps, 1) irreversible oxidation of Ni → Ni(OH)<sub>2</sub>, which consumes OH<sup>-</sup> anions on the cathode surface, and 2) reversible Ni(OH)<sub>2</sub> ⇌ NiOOH. The irreversible step was confirmed by the ‘gradually’ decreasing peak intensity for Ni (111) and growing intensity for peak intensity related to Ni(OH)<sub>2</sub> in XRPD patterns during battery charging (**Supplementary Figs. 15a-b, Eqn. S1**). However, following charging to > 1.8 V, the peak exhibiting Ni(OH)<sub>2</sub> vanished and a new peak related to NiOOH appeared, evidencing the transformation of Ni<sup>2+</sup> to Ni<sup>3+</sup> (**Supplementary Figs. 15b-c**). Additionally, this reaction generates H<sup>+</sup> to initiate a H<sub>3</sub>O<sup>+</sup>-rich local environment (**Eqn. S2**). NiOOH can be reduced to Ni(OH)<sub>2</sub> following discharging where it is beneficial to dynamically maintain the H<sub>3</sub>O<sup>+</sup>-rich local environment. As seen in **Supplementary Fig. 18**, the specific capacity for Ni/C is *ca.* 150 mAh g<sup>-1</sup>. The Ni in the coating is < 0.1 mg cm<sup>-2</sup> and the electrode loading is *ca.* 10 mg cm<sup>-2</sup>. Therefore the capacity provided by the Ni/C is < 1.5 mAh g<sup>-1</sup>.

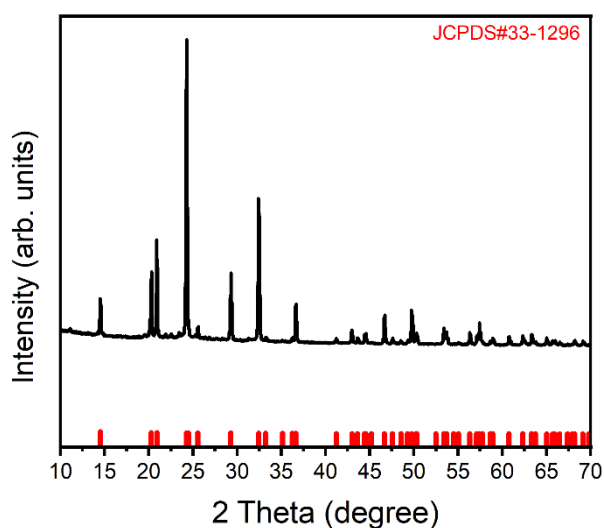


The oxidation of Ni and reversible transformation between Ni(OH)<sub>2</sub> and NiOOH were confirmed *via* soft XAS. As shown in **Supplementary Fig. 19**, Ni has the greater spectral mass in two locations in the L<sub>3</sub> edge absorption band (peak A in the lower, and peak B in the higher energy region). The intensity ratio peak B/peak A is good evidence for state changes in Ni element<sup>1,2</sup>. An increase in the intensity ratio evidences the oxidation of Ni, whilst a decrease evidences the reduction of Ni. In the pristine state, the average oxidation state for Ni will be close to Ni<sup>0</sup>. Following charging to 2.2 V, the ratio peak B/peak A increases, confirming the oxidation of Ni. However, following discharging to 0.5 V, the intensity ratio decreases, evidencing that Ni oxidation and reduction are partially reversible during battery cycling.

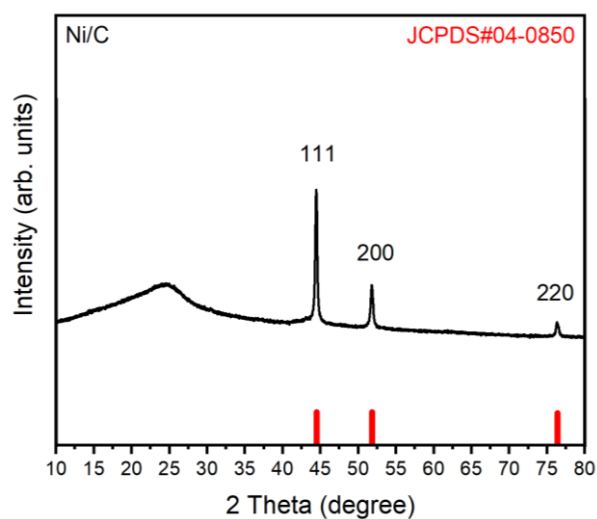
## Supplementary Figures



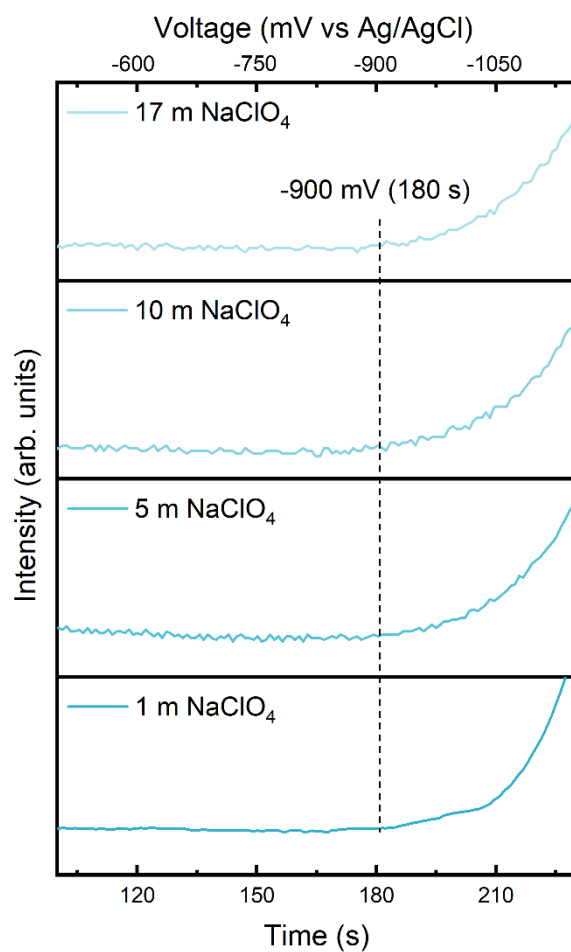
**Supplementary Fig. 1 | X-ray diffraction (XRD) pattern for Na<sub>2</sub>MnFe(CN)<sub>6</sub> (NMF) cathode.** The pattern confirms crystallinity for NMF in good agreement with reported findings<sup>3</sup>.



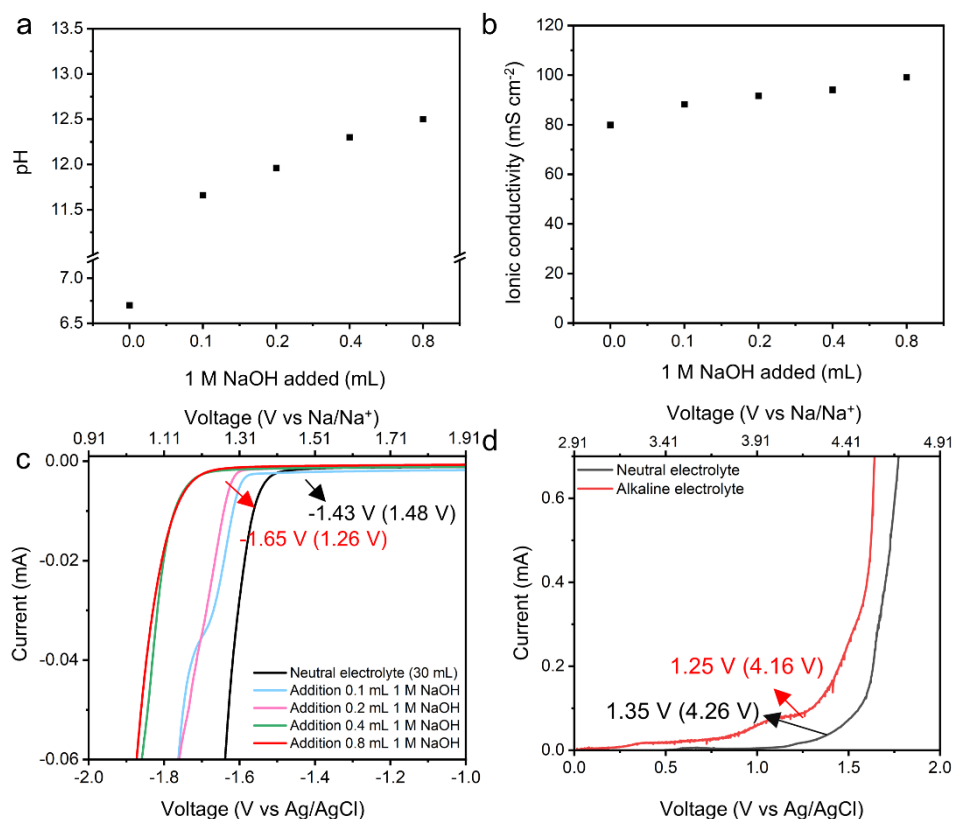
**Supplementary Fig. 2 | XRD pattern for NaTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> (NTP) anode.** The pattern for synthesized NTP anode agrees well with the Powder Diffraction File (PDF) standard card for NaTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>.



**Supplementary Fig. 3 | XRD pattern for Ni/C.** The pattern confirms hybrid of Ni/C.

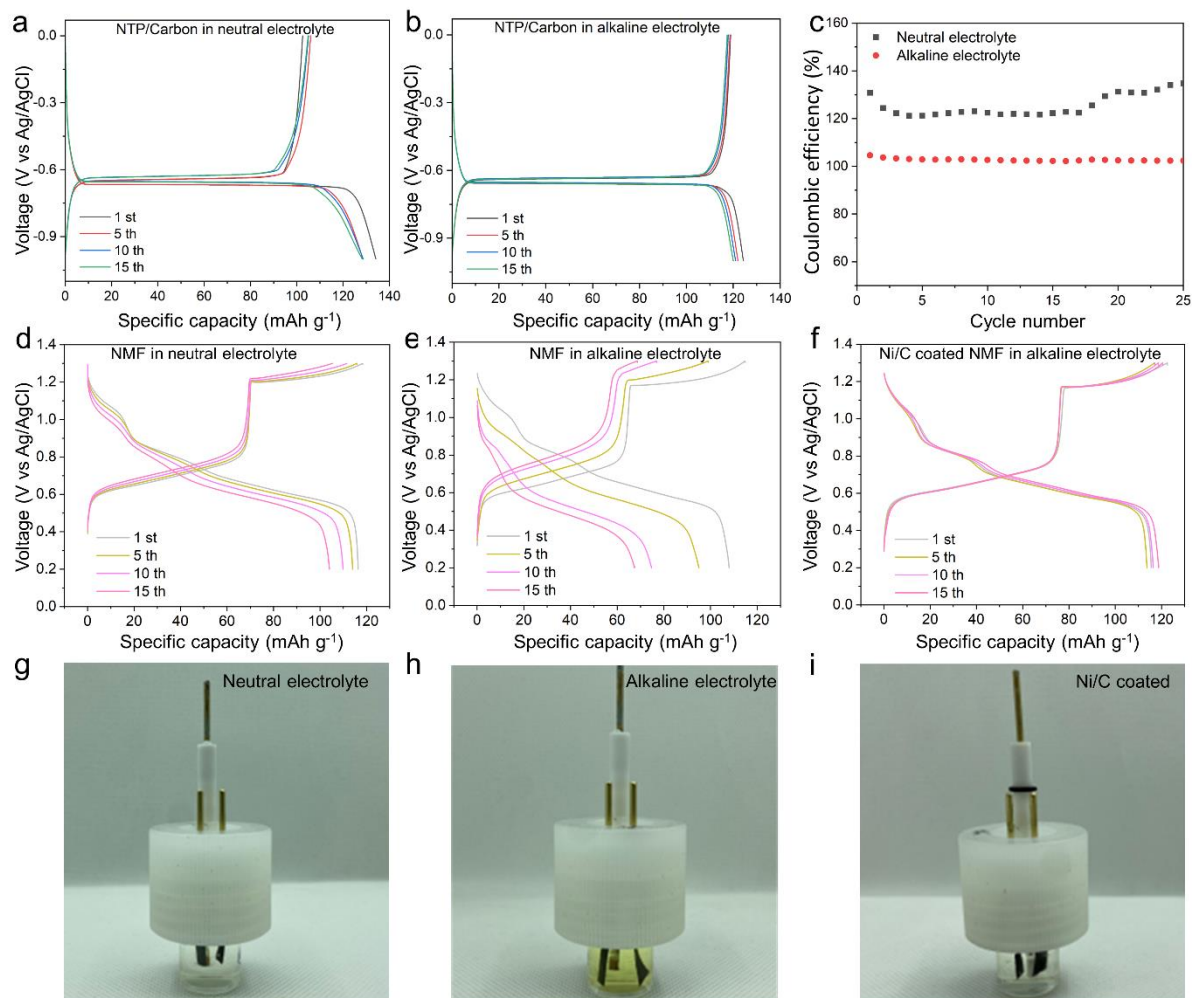


**Supplementary Fig. 4 | *In-situ* DEMS tests for NaClO<sub>4</sub> electrolytes at a rate of 5 mV s<sup>-1</sup>.** Au-coated PTFE as the working electrolyte, Pt-wire as the counter electrode and Ag/AgCl as the reference electrode.

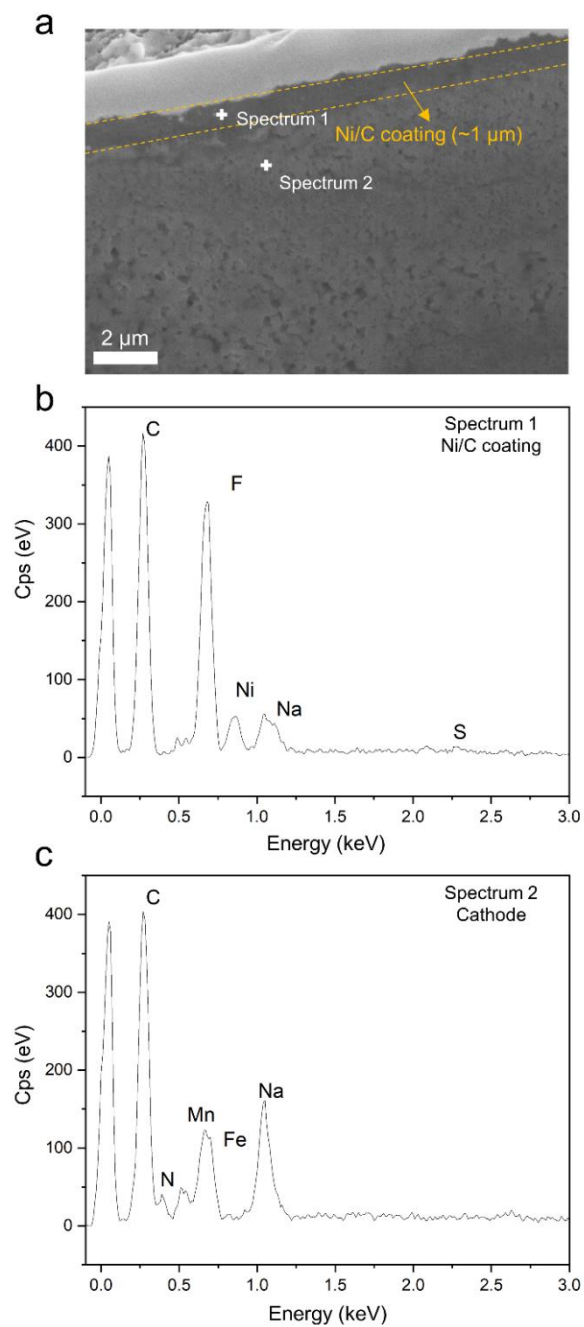


**Supplementary Fig. 5 | Electrolyte characterization using three-electrode system** (with glass carbon as the working electrode, Ti as the counter electrode, and Ag/AgCl as the reference electrode). **a**, pH for neutral electrolyte following the addition of selected volumes of 1 M NaOH. **b**, Ionic conductivity for neutral electrolytes following the addition of selected volumes of 1 M NaOH. **c**, LSV curves for electrolytes with NaOH addition from -1.0 to -2.0 V. **d**, LSV curves for different electrolytes from 0 to 2.0 V.

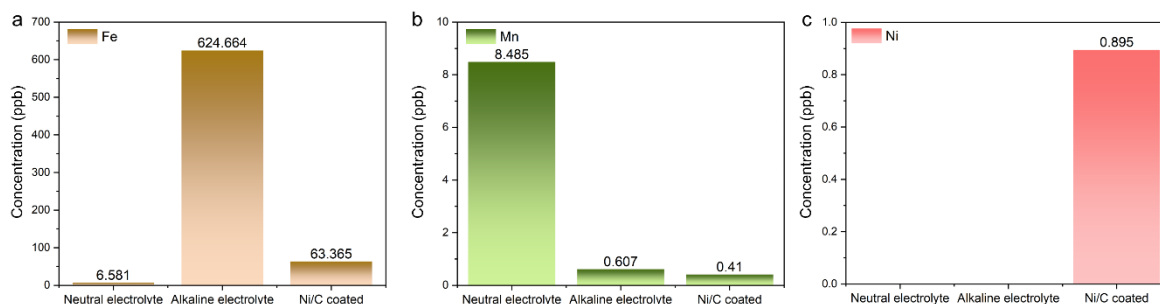
As evidenced in **Supplementary Figs. 5a-b**, with the addition of 1 M NaOH (from 0 to 0.8 mL), the pH and ionic conductivity for the electrolyte (30 mL) increase, which lowers cathodic limiting potential (**Supplementary Fig. 5c**). From LSV curves in **Supplementary Fig. 5c**, the electrolyte with 0.4 mL NaOH addition exhibits similar HER overpotential to that with 0.8 mL NaOH addition. The alkaline system with 0.4 mL NaOH addition was therefore selected as an example. However, the increased alkalinity with 0.4 mL 1 M NaOH addition boosted OER at the cathode (**Supplementary Fig. 5d**).



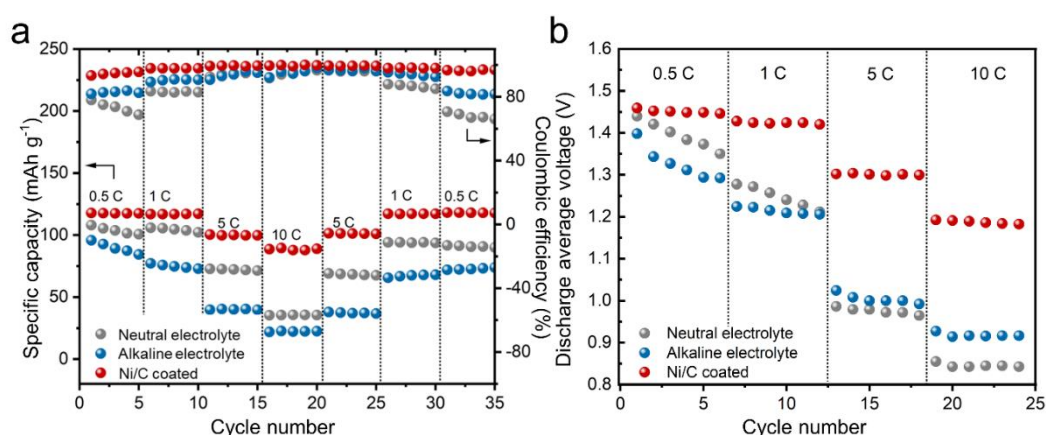
**Supplementary Fig. 6 | Cycling performance for half-cell using three-electrode system** (Ag/AgCl electrode with sat. aq. KCl solution as reference electrode and carbon black as counter electrode). Charge and discharge profiles for NTP electrode in a three-electrode cell using **a**, Neutral and **b**, Alkaline electrolyte. **c**, Coulombic efficiency (CE) comparison for NTP electrode in a three-electrode cell using neutral and alkaline electrolyte. Charge and discharge profiles for NMF electrode in **d**, Neutral and **e**, Alkaline, electrolyte and **f**, Alkaline electrolyte with Ni/C coating. Digital photograph of cycled NMF electrode in a three-electrode system using **g**, Neutral and **h**, Alkaline, electrolyte and **i**, Alkaline electrolyte (NMF with Ni/C coating).



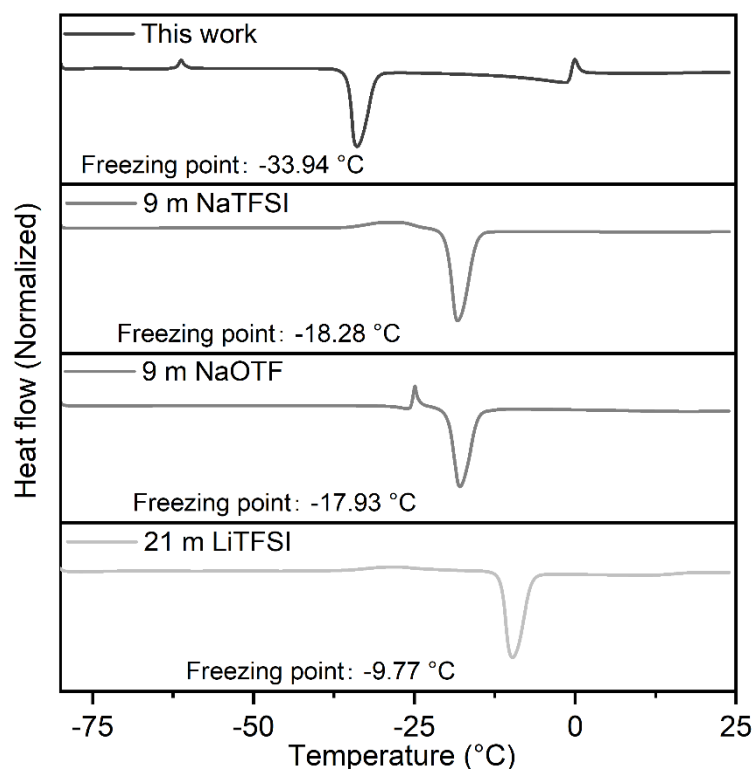
**Supplementary Fig. 7 | Interface structure characterization of coated cathode. a,** Cross-section SEM image of Ni/C coated NMF. **b-c,** EDS point scan for cross-section SEM image.



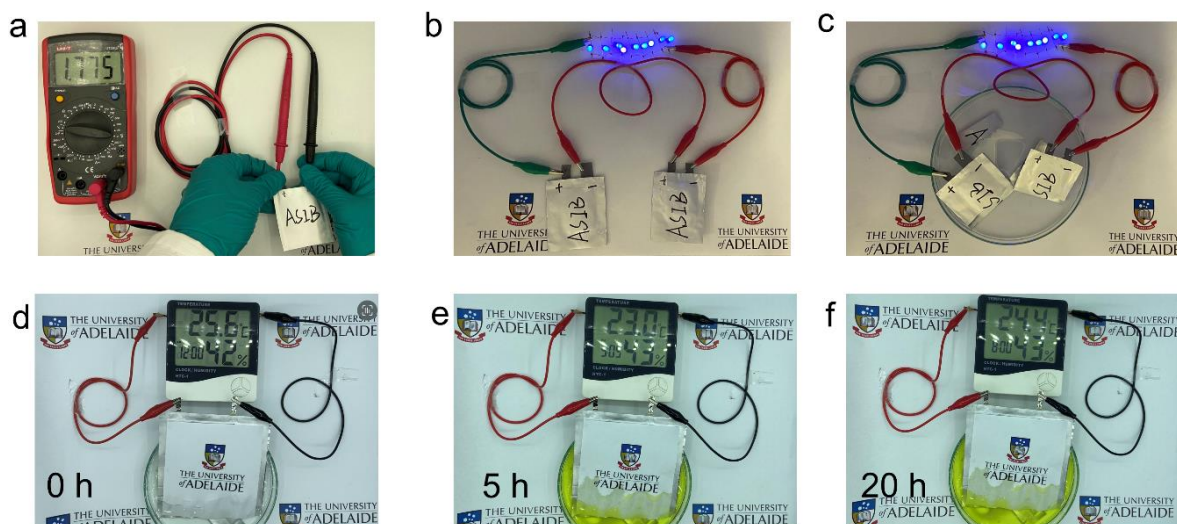
**Supplementary Fig. 8 | ICP-MS findings for electrolytes collected from three-electrode cells after cycling with/without Ni/C coating on the cathode surface in neutral/alkaline electrolyte. a, Fe, b, Mn and c, Ni, concentration.**



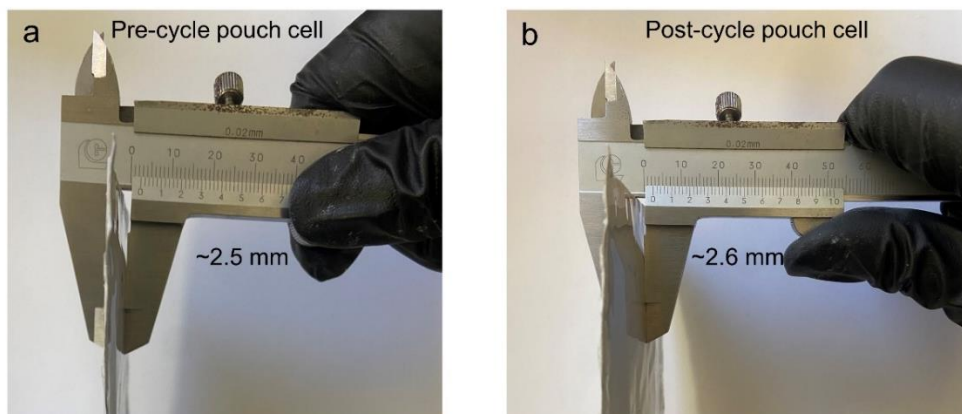
**Supplementary Fig. 9 | Electrochemical performance for NMF//NTP full cell. a, Rate capability and corresponding CE for three NMF//NTP cells with, neutral, alkaline and alkaline (with Ni/C coated) electrolytes. b, Comparison of average discharge voltage for three cells at varying rates.**



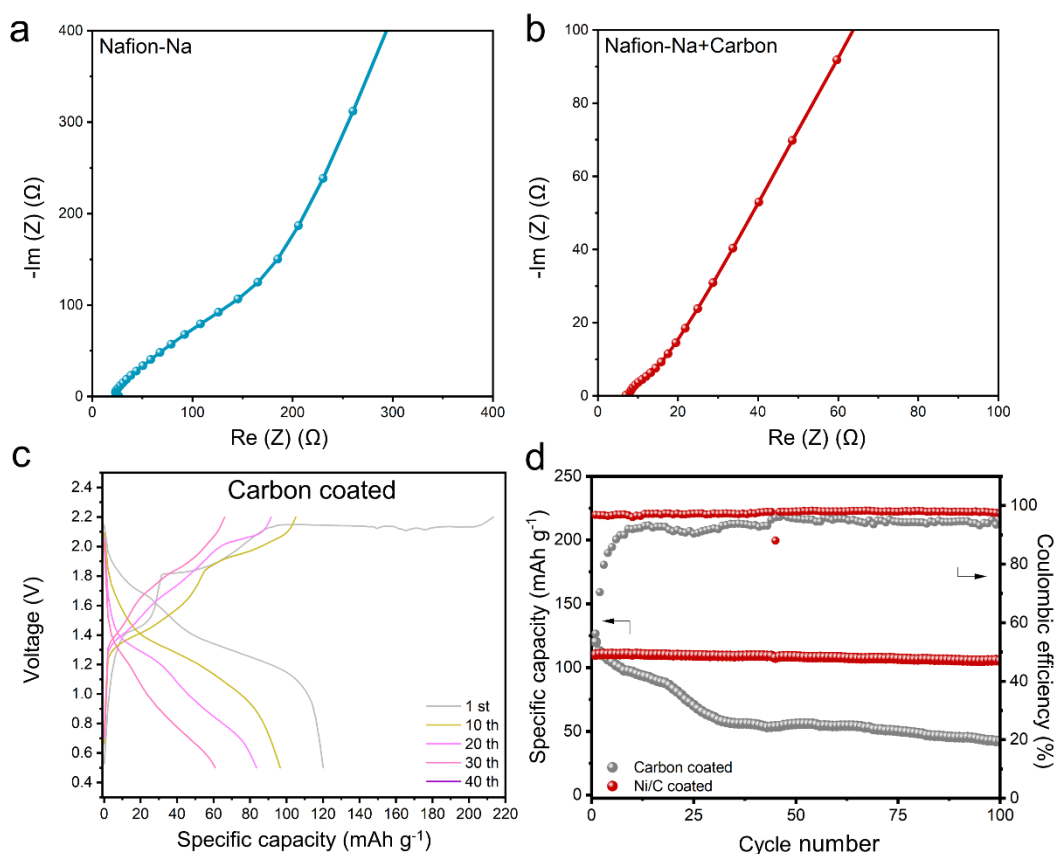
**Supplementary Fig. 10 | Differential scanning calorimetry (DSC) for selected electrolytes.** Electrolyte in this work exhibits lowest freezing point of  $-33.94\text{ }^{\circ}\text{C}$  compared with commonly used electrolytes, 9 m NaTFSI, 9 m NaOTF and 21 m LiTFSI.



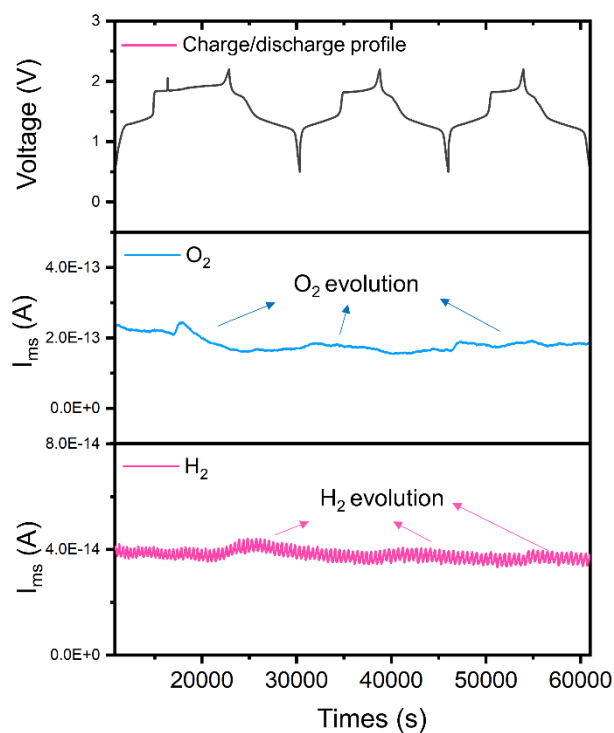
**Supplementary Fig. 11 | Testing for safety risks with NMF//NTP pouch cell.** **a**, Output voltage for pouch cell. **b**, Digital photograph of blue-color LED lights powered by two NMF//NTP pouch cells. **c**, Digital photograph of cut pouch cells, powered blue-color lights in water. **d-f**, A cut pouch cell following recharge powering humidity clock in water for  $> 20\text{ h}$ .



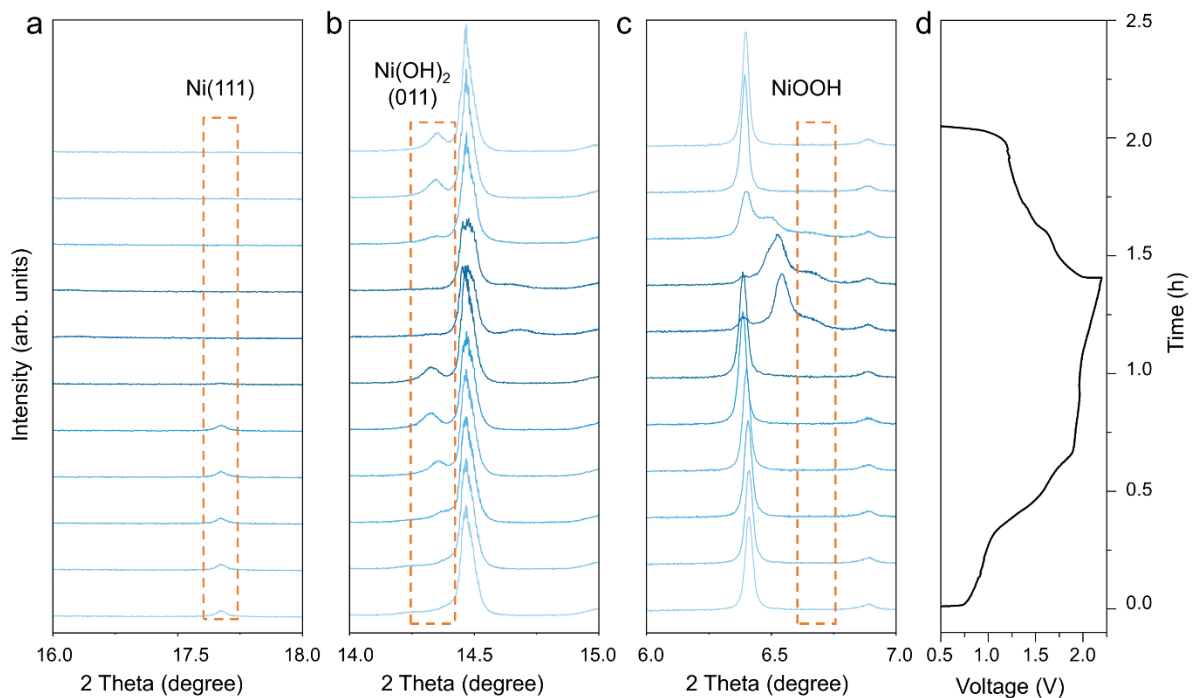
**Supplementary Fig. 12 | Digital photograph of pouch cell.** Thickness of pouch cell **a**, Before, and **b**, Following cycling.



**Supplementary Fig. 13 | Function of carbon in coating.** EIS spectra for **a**, Nafion-Na and **b**, Nafion-Na and 25 m/m% carbon in Nafion-Na (following addition of 10  $\mu\text{L}$  alkaline electrolyte) using stainless steel//coating//stainless steel cell configuration. **c**, Charge/discharge profiles for NMF//NTP full cell following coating carbon. **d**, Comparison of cycling performance for NMF//NTP full cell following coating carbon with that following coating Ni/C in alkaline electrolyte.



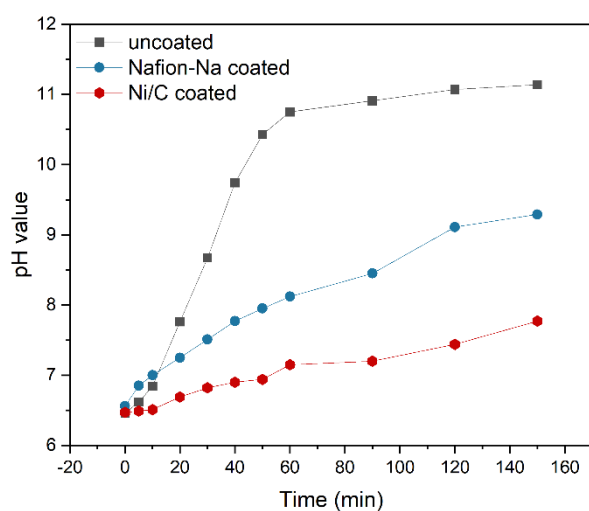
**Supplementary Fig. 14 Operando DEMS to determine H<sub>2</sub> and O<sub>2</sub> evolution during NMF//NTP battery cycling in neutral electrolyte at 0.5 C (Voltage range 0.5 to 2.2 V).**



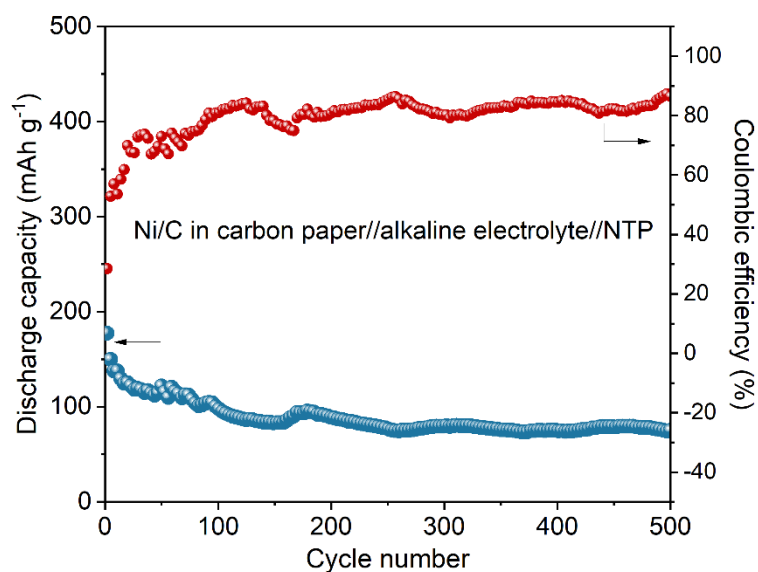
**Supplementary Fig. 15 | Operando synchrotron XRPD ( $\lambda = 0.5903$ ) for NMF//NTP full cells with Ni/C coating in range 0.5 to 2.2 V. a, b and c, XRPD patterns for Ni/C coated NMF cathode during 1<sup>st</sup> charge/discharge and d, Corresponding charge/discharge profile (right).**



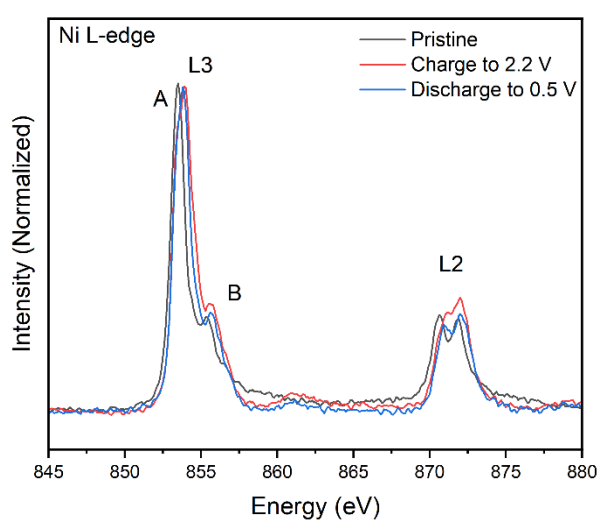
**Supplementary Fig. 16 | Digital photograph of the H-cell to test barrier effect of coatings.**



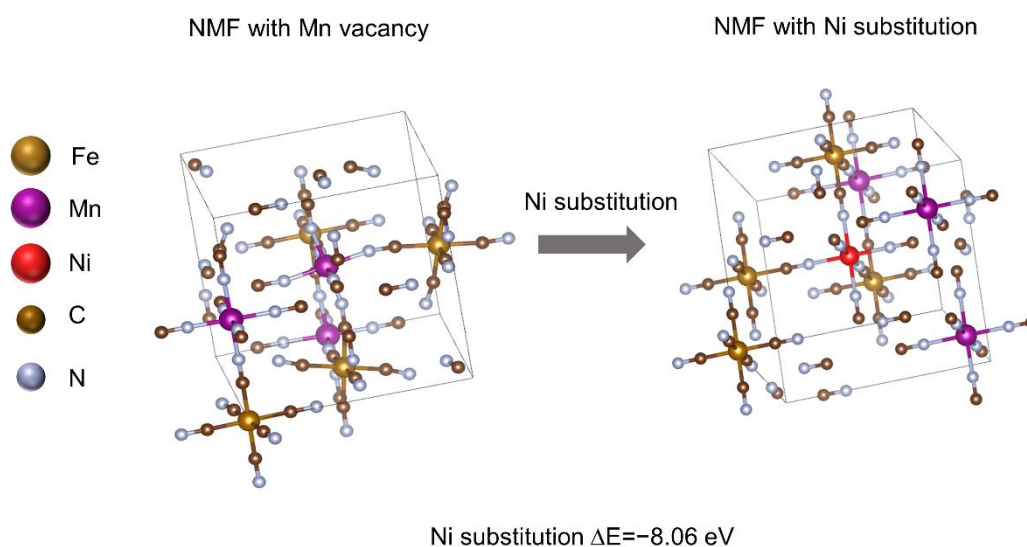
**Supplementary Fig. 17 | Increasing pH rate in  $\text{OH}^-$  penetration tests using H-cells.**



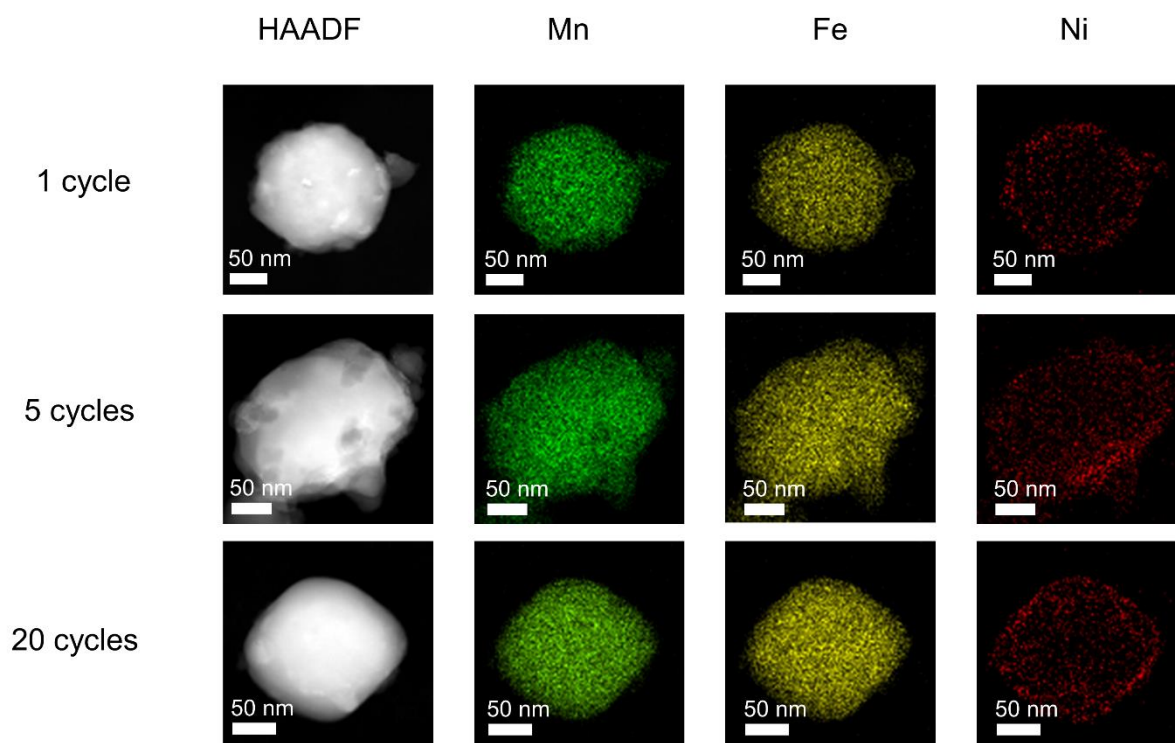
**Supplementary Fig. 18 | Cycling performance for Ni/C//alkaline electrolyte//NTP full batteries (pre-cycled for 1 cycle).**



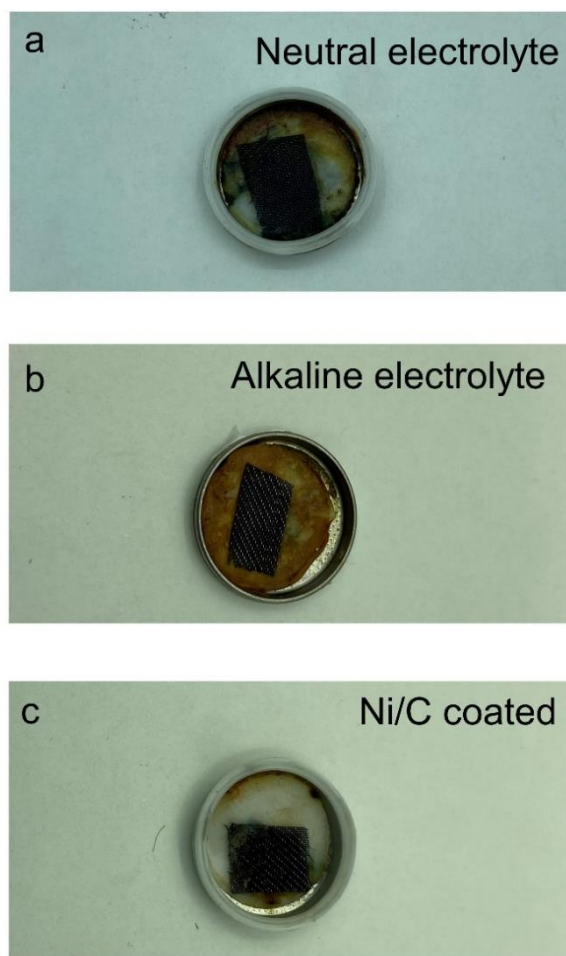
**Supplementary Fig. 19 | Soft XAS spectra for Ni/C coated NMF cathode in pristine state, charged to 2.2 V, and discharged to 0.5 V (Ni L-edge).**



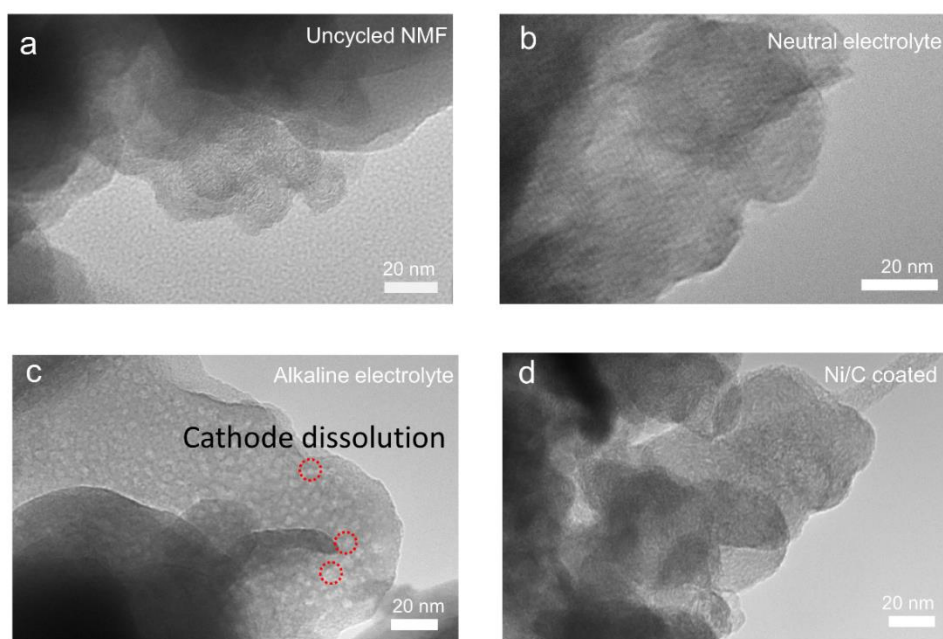
**Supplementary Fig. 20 | DFT computations for Ni substitution energy *via* comparing energy of NMF with a Mn vacancy and NMF with Ni substitution.**



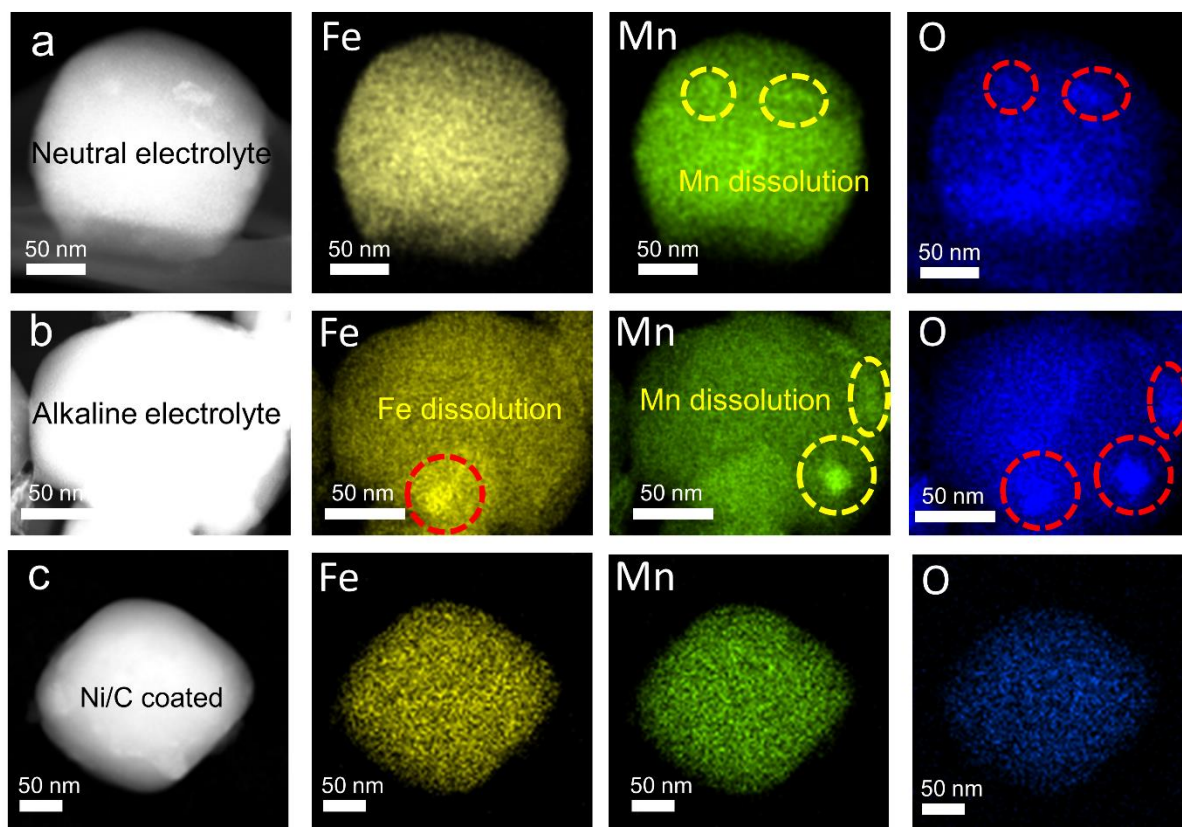
**Supplementary Fig. 21 | STEM-EDS mapping for NMF particles with Ni/C coating cycled in alkaline electrolyte following 1<sup>st</sup>, 5<sup>th</sup> and 20<sup>th</sup> cycle.**



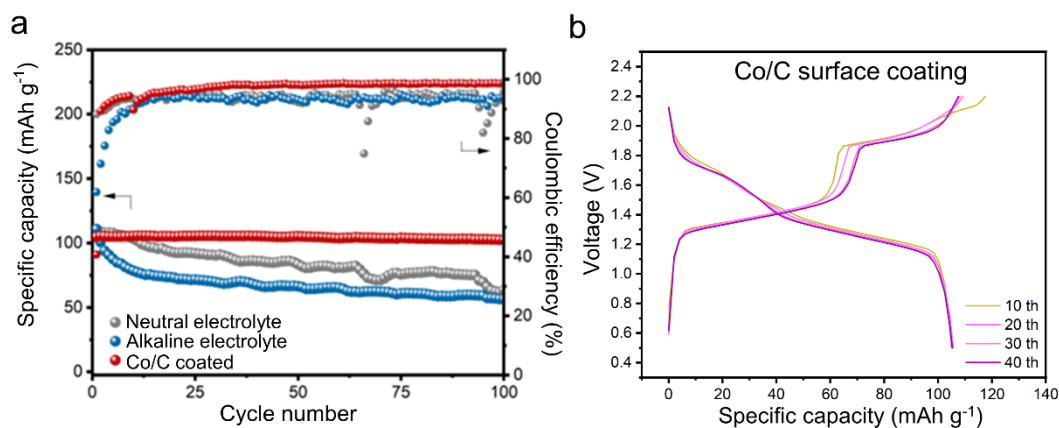
**Supplementary Fig. 22 | Digital photographs of cycled batteries.** Digital photographs of cycled coin cells in **a**, Neutral **b**, Alkaline and **c**, Alkaline electrolyte with Ni/C coating.



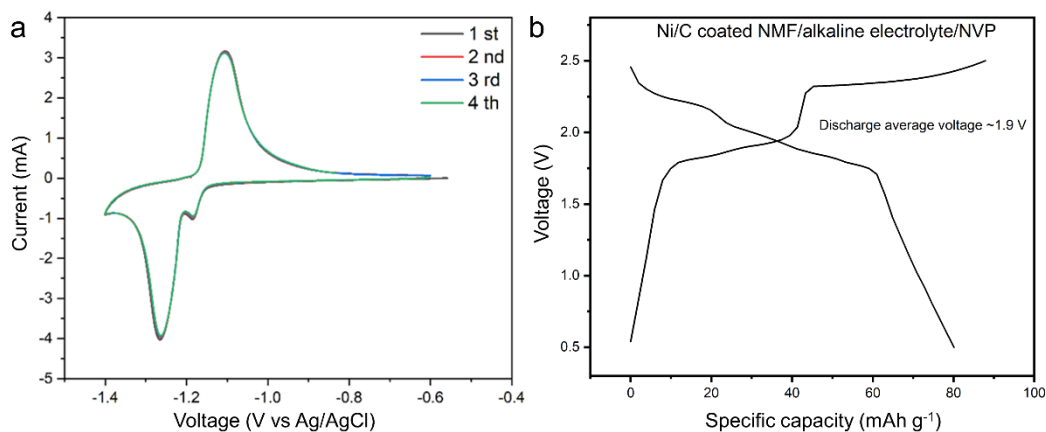
**Supplementary Fig. 23 | TEM images of uncycled NMF and cycled NMF.** **a**, Uncycled NMF. **b**, NMF cycled in neutral electrolyte. **c**, NMF cycled in alkaline electrolyte. **d**, Ni/C coated NMF cycled in alkaline electrolyte.



**Supplementary Fig. 24 | STEM-EDS mapping for cycled NMF electrode.** Electrode cycled in **a**, Neutral electrolyte **b**, Alkaline electrolyte and **c**, Ni/C coating.



**Supplementary Fig. 25 | Cycling performance for NMF//NTP full cells with Co/C coating in alkaline electrolyte. a,** Cycling performance for NMF//NTP full cells in selected systems at 1 C with NMF cathode coated with Co/C. **b,** Charge/discharge curves for NMF//NTP cells with NMF cathode coated with Co/C.



**Supplementary Fig. 26 | Electrochemical performance for Ni/C coated NMF/Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>@C in alkaline electrolyte. a,** CV curves for Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>@C using three-electrode with Ag/AgCl with sat. KCl solution as the reference electrode, and carbon black as the counter electrode. **b,** Charge/discharge profiles for Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>@C/NMF full cell with Ni/C coating.

## Supplementary Tables

**Supplementary Table 1 | Viscosity and pH for selected electrolytes.**

| Electrolyte                                         | pH   | Viscosity<br>(mPa·s) |
|-----------------------------------------------------|------|----------------------|
| This work                                           | 12.3 | 6.0 at 23.5 °C       |
| 21 m LiTFSI (Tested in this work)                   | ~7   | 46.8 at 23.5 °C      |
| 9 m Na CF <sub>3</sub> SO <sub>3</sub> <sup>4</sup> | ~7   | 4.5 at 25 °C         |
| 22 m KCF <sub>3</sub> SO <sub>3</sub> <sup>4</sup>  | ~7   | 6.5 at 25 °C         |
| 9 m NaOTF + 22 m TEAOTF <sup>5</sup>                | ~7   | 30.2 at 25 °C        |
| 8 m LiOAc +32 m KOAc <sup>6</sup>                   | ~9   | 374 at 25 °C         |
| 19.4 m LiTFSI + 8.3 m LiBETI <sup>7</sup>           | ~7   | 203 at 30 °C         |

**Supplementary Table 2 | Comparison of lifespan and energy density of this work with reported aqueous Na full batteries.**

| Battery                                                                                                                                        | Energy density <sup>a</sup><br>(Wh kg <sup>-1</sup> ) | Mean voltage<br>(V) | Cycling life<br>(Capacity retention, Cycles,<br>Rate)  |
|------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------|---------------------|--------------------------------------------------------|
| This work                                                                                                                                      | ~88.9                                                 | 1.46                | ~100 %, 200 cycles, 1 C<br>74.3 %, 13,000 cycles, 10 C |
| NMF//polymer electrolyte//NTP <sup>13</sup>                                                                                                    | 86                                                    | 1.36                | 80 %, 4,000 cycles, 10 C                               |
| NMF//eutectic electrolyte//NTP <sup>14</sup>                                                                                                   | ~80                                                   | 1.35                | 74.5 %, 1,000 cycles, 4.2 C                            |
| Na <sub>1.88</sub> Mn[Fe(CN) <sub>6</sub> ] <sub>0.97</sub> ·1.35H <sub>2</sub> O//<br>NaTiOPO <sub>4</sub> <sup>5</sup>                       | 71                                                    | 1.74                | 76 %, 800, 1 C                                         |
| Na <sub>3</sub> V <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub> // Na <sub>3</sub> V <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub> <sup>15</sup> | 70                                                    | 1.75                | 87.5 %, 100, 1 C                                       |
| NaCoHCF//NTP <sup>16</sup>                                                                                                                     | 67                                                    | 1.33                | 98 %, 100 cycles, 5 C                                  |
| Na <sub>3</sub> (VOPO <sub>4</sub> ) <sub>2</sub> F//NTP <sup>17</sup>                                                                         | 64                                                    | 1.44                | 77 %, 500 cycles, 1 C                                  |
| NMF//17 m NaClO <sub>4</sub> //NTP <sup>18</sup>                                                                                               | ~60                                                   | 1.3, 1.8            | ~60 %, 100 cycles, 2 mA cm <sup>-2</sup>               |
| Na <sub>2</sub> MnFe(CN) <sub>6</sub> //KMnCr(CN) <sub>6</sub> <sup>19</sup>                                                                   | 58                                                    | 1.6                 | 75 %, 100 cycles, 30 C                                 |
| Na <sub>2</sub> Zn <sub>3</sub> Fe(CN) <sub>6</sub> //NTP <sup>20</sup>                                                                        | 55                                                    | 1.6                 | 100 %, 1,000 cycles, 10 C                              |
| NaCuHCF//NTP <sup>21</sup>                                                                                                                     | 48                                                    | 1.4                 | 88 %, 1,000 cycles, 10 C                               |
| Na <sub>2</sub> NiFe(CN) <sub>6</sub> //NTP <sup>22</sup>                                                                                      | 42.5                                                  | 1.47                | 88 %, 100 cycles, 5 C                                  |
| Na <sub>3</sub> MnTi(PO <sub>4</sub> ) <sub>3</sub> // Na <sub>3</sub> MnTi(PO <sub>4</sub> ) <sub>3</sub> <sup>23</sup>                       | 40                                                    | 1.4                 | 98 %, 250 cycles, 1 C                                  |
| K <sub>0.27</sub> MnO <sub>2</sub> //NTP <sup>24</sup>                                                                                         | 34                                                    | 0.8                 | 80 %, 100 cycles, 1 C                                  |
| Na <sub>3</sub> V <sub>2</sub> O <sub>2x</sub> (PO <sub>4</sub> ) <sub>2</sub> F <sub>3-2x</sub> //NTP <sup>25</sup>                           | 31                                                    | 1.47                | 75 %, 400 cycles, 10 C                                 |
| Na <sub>0.66</sub> Mn <sub>0.66</sub> Ti <sub>0.44</sub> O <sub>2</sub> //NTP <sup>26</sup>                                                    | 31                                                    | 1                   | 92.7 %, 1,200 cycles, 1 C                              |
| NaMnO <sub>2</sub> //NTP <sup>27</sup>                                                                                                         | 30                                                    | 0.81                | 75 %, 500 cycles, 10 C                                 |

<sup>a</sup> Based on the total mass of cathode and anode, the mass of Ni/C has been included in this work.

**Supplementary Table 3 | Data for computation of cell-level energy density.**

| Cell component | Parameter                  | Type/amount        | Unit                |
|----------------|----------------------------|--------------------|---------------------|
| Cathode        | Active material (AM)       | NMF                |                     |
|                | AM capacity                | 116                | mAh g <sup>-1</sup> |
|                | Coating mass               | 0.03               | g cm <sup>-2</sup>  |
|                | Loading                    | 95.50 %            |                     |
|                | Binder                     | PTFE <sup>1</sup>  |                     |
|                | Conductive agent           | Super P            |                     |
|                | Ni/C coating               | 1 %                |                     |
|                | Current collector          | Ti foil            |                     |
|                | Thickness                  | 6                  | μm                  |
| Anode          | Active material (AM)       | NTP                |                     |
|                | AM capacity                | 120                | mAh g <sup>-1</sup> |
|                | coating mass               | 0.03070845         | g cm <sup>-2</sup>  |
|                | Loading                    | 96.50 %            |                     |
|                | Binder                     | PTFE               |                     |
|                | Conductive agent           | Super P            |                     |
|                | Current collector          | Ti foil            |                     |
|                | Thickness                  | 6                  | μm                  |
| Electrolyte    | Salt                       | NaClO <sub>4</sub> |                     |
|                | Solvent                    | H <sub>2</sub> O   |                     |
|                | Electrolyte/Capacity Ratio | 2.5                | g Ah                |
| Separator      | Celgard                    |                    |                     |
|                | Mass                       | 1.09               | mg cm <sup>-2</sup> |
|                | Length                     | 10.6               | cm                  |
|                | Width                      | 10.6               | cm                  |
| Cell geometry  | Size of CE <sup>2</sup>    | 10*10              | cm <sup>2</sup>     |
|                | Size of AE <sup>3</sup>    | 10.3*10.3          | cm <sup>2</sup>     |
|                | Size of tabs               | 1                  | cm <sup>2</sup>     |
|                | Size of Separator          | 10.6*10.6          | cm <sup>2</sup>     |
|                | N/P Ratio                  | 1.07               |                     |
|                | Size of Al-plastic film    | 12.6*25.2          | cm <sup>2</sup>     |
|                | Cathode Layers             | 10                 |                     |
|                | Anode Layers               | 11                 |                     |
|                | Separator Layers           | 22                 |                     |
|                | Mass of Ni Tabs            | 0.2167             | g cm <sup>-2</sup>  |
|                | Number of Ni Tabs          | 2                  | ea                  |
| Cell           | Output Voltage             | 1.46               | V                   |
|                | Capacity                   | 6.64               | Ah                  |
|                | Total mass                 | 159                | g                   |
|                | Energy density             | 61.0               | Wh kg <sup>-1</sup> |

<sup>1</sup> PTFE: polytetrafluoroethylene

<sup>2</sup> CE: cathode electrode

<sup>3</sup> AE: anode electrode

**Supplementary Table 4 | Comparison of this work with selected commercial batteries.**

| Battery                                        | Element abundance (ppm) | Lifespan (Cycles)     | Energy density (Wh kg <sup>-1</sup> ) | Safety | Environmental benignity | Cost-efficacy |
|------------------------------------------------|-------------------------|-----------------------|---------------------------------------|--------|-------------------------|---------------|
| This work                                      | Fe (41000)              | 1,3000                | ~50                                   | High   | High                    | High          |
|                                                | Mn (950)                |                       |                                       |        |                         |               |
|                                                | Na (23000)              |                       |                                       |        |                         |               |
|                                                | Ti (5600)               |                       |                                       |        |                         |               |
|                                                | Ni (80)                 |                       |                                       |        |                         |               |
| Lead-acid <sup>28</sup>                        | Pb (14)                 | 300-1,000             | 25-40                                 | High   | Low                     | High          |
| Ni-MH <sup>29</sup>                            | Ni (80)                 | 200-1,200             | 50-85                                 | Medium | Medium                  | Medium        |
|                                                | La (32)                 |                       |                                       |        |                         |               |
| Li-ion <sup>30</sup> (LFP/graphite)            | Li (20)                 | 160-2,000             | 160                                   | Low    | Medium                  | Medium        |
| Super-capacitor <sup>29</sup>                  | C (480)                 | 5,000-10 <sup>5</sup> | 5-10                                  | High   | High                    | Low           |
| Flow battery <sup>28</sup><br>(Vanadium redox) | V (120)                 | 5,000-10 <sup>4</sup> | 10-25                                 | High   | Low                     | Medium        |

**Supplementary Table 5 | Adsorption energy for adsorbed H, OH and H<sub>2</sub>O at most stable adsorption sites on (200) and (111) facets of Ni nanoparticles under differing electro-potential.**

| Voltage<br>(V vs. SHE) | Facet (2 0 0)     |       |      | Facet (1 1 1)     |       |       |
|------------------------|-------------------|-------|------|-------------------|-------|-------|
|                        | *H <sub>2</sub> O | *OH   | *H   | *H <sub>2</sub> O | *OH   | *H    |
| 0.0                    | -0.53             | -1.17 | 0.61 | -1.61             | -2.52 | -4.21 |
| 0.5                    | -0.62             | -1.25 | 0.28 | -1.12             | -1.81 | -0.86 |
| 1.0                    | -0.41             | -1.08 | 0.33 | -1.13             | -1.72 | 0.90  |

**Supplementary Table 6 | Elemental atomic fraction based on EDS mapping for NMF following different cycles.**

| Cathode                                                                        | Fe<br>(% <sup>a</sup> ) |                 | Mn<br>(% <sup>a</sup> ) |                 | Ni<br>(% <sup>a</sup> ) |                 |
|--------------------------------------------------------------------------------|-------------------------|-----------------|-------------------------|-----------------|-------------------------|-----------------|
|                                                                                | Atomic<br>fraction      | Atomic<br>error | Atomic<br>fraction      | Atomic<br>error | Atomic<br>fraction      | Atomic<br>error |
| NMF with Ni/C<br>following cycling in<br>alkaline electrolyte<br>for 1 cycle   | 44.63                   | 7.64            | 53.19                   | 6.00            | 2.18                    | 0.40            |
| NMF with Ni/C<br>following cycling in<br>alkaline electrolyte<br>for 5 cycles  | 44.70                   | 7.66            | 53.24                   | 6.01            | 2.06                    | 0.38            |
| NMF with Ni/C<br>following cycling in<br>alkaline electrolyte<br>for 20 cycles | 45.00                   | 7.73            | 53.05                   | 6.02            | 1.95                    | 0.36            |

<sup>a</sup> Total amount of Fe, Mn and Ni was normalized to 100 %.

**Supplementary Table 7 | Detailed structural information on samples cycled for 1<sup>st</sup> cycle following Rietveld refinement.**

| Sample                                                                  | a =b=c (Å) | $\alpha=\beta=\gamma$ | Volume<br>(Å <sup>3</sup> ) | Size<br>(μm) | R <sub>wp</sub><br>(%) |
|-------------------------------------------------------------------------|------------|-----------------------|-----------------------------|--------------|------------------------|
| NMF cathode following cycling in<br>alkaline electrolyte                | 5.26358    | 90°                   | 145.829                     | 0.0454       | 5.36                   |
| Ni/C coated NMF cathode<br>following cycling in alkaline<br>electrolyte | 5.28161    | 90°                   | 147.333                     | 0.2229       | 5.35                   |

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