# **Supporting Information**

Nanozeolite ZSM-5 electrolyte additive for long life sodiumion batteries

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## **1. Experimental Section**

#### Electrolyte preparation

The standard electrolyte, 1 M NaPF<sub>6</sub> in EC : DEC (1/1, V/V) and the electrolyte with FEC additives, 1M NaPF<sub>6</sub> in EC: DEC: FEC (5.3 wt% FEC) were both purchased from Flurochem. 0.1 wt% NZeo additive (NanoH-ZSM-5 P91, ACS Materials) was added and dispersed in the standard electrolyte. The NZeo was dried in a vacuum oven at 100 °C for 2 hr before use. All the electrolyte preparation processes are completed in the glovebox (H<sub>2</sub>O <0.1ppm, O<sub>2</sub> <0.1ppm).

## Electrochemical measurements of Na<sub>a</sub>MO<sub>2</sub>/C full cells

The Na<sub>*a*</sub>[Ni<sub>*w*</sub>Mn<sub>*x*</sub>Mg<sub>*y*</sub>Ti<sub>*z*</sub>]O<sub>2</sub> (Na<sub>*a*</sub>MO<sub>2</sub>) a mixed P2-O3 type oxide material<sup>1,2</sup> was made into an electrode with 92 wt% active material, 5 % conductive additive and 3 % PVDF binder using a slurry cast process. The hard carbon negative electrode contained (88 wt% active material : 9 wt% PVDF binder : 3 wt% carbon black). All the electrodes were dried in a vacuum oven at 120 °C overnight prior to being transferred into a glovebox.

For the full cell assembly process, the mass balancing of positive and negative electrode were calculated based on the  $(N/P)_Q$  capacity ratio 1.1:1. The electrochemical performance of the full cells were evaluated in 2032-type coin cell, with Na<sub>a</sub>MO<sub>2</sub> cathode (12 mg/cm<sup>2</sup>), hard carbon anode (5 mg/cm<sup>2</sup>), separated by Celgard polymer containing enough electrolyte to wet the components (~75µl). Each electrochemical test was performed using three independently produced cells to show standard deviations.

Three-electrode Swagelok cells were also built to examine the potential of each electrode. Similar to the full cell assembly in the coin cell type, in the three-electrode cell system, a  $Na_aMO_2$  cathode and a hard carbon anode with diameter 12 mm were separated with a layer of glass-fibre (GFA Whatman) and Celgard polymer with 90  $\mu$ l of electrolytes. Additionally, a sodium metal disc was introduced in the system as a reference electrode, separated using a glass fibre separator.

#### Surface characterisation

After completion of cycling the cell was disassembled in a glovebox under an argon atmosphere. Scanning electron microscopy with a field-emission SEM microscope (Sigma, Carl Zeiss, Germany) equipped with an energy-dispersive spectrometer (EDS) (Xmax 50, Oxford Instruments) was used to characterize the surface of the electrodes after cycling. SEM images were captured at 10 kV (1.6 nA) when a high-performance ion conversion and electron detector was employed, or 20 kV (8.0 nA) when a secondary electron detector was employed.

X-ray photoelectron spectroscopy (XPS) measurements<sup>3-7</sup> were carried out using a Kratos Axis Ultra DLD spectrometer (Kratos Analytical, Manchester, UK). Samples were prepared in an argon glovebox, mounted on to a copper stub and transferred to the spectrometer using an inert transfer unit under an argon atmosphere with no exposure to air. Once an acceptable vacuum level had been reached, the samples were transferred to the main analysis chamber. The samples were illuminated by a monochromated Al K $\alpha$  X-ray source (h $\nu$  = 1486.7 eV) and also flooded with low energy electrons from a charge neutraliser in order to prevent the surface from becoming positively charged during the experiment. Data were collected in a hemispherical analyser using a pass energy of 160 eV for survey spectra and 20 eV for high resolution core level spectra (resolution approximately 0.4 eV). Data were analysed using the CasaXPS software package, using mixed Gaussian-Lorentzian (Voigt) lineshapes, asymmetry parameters where appropriate and Shirley backgrounds. The spectrometer was calibrated using the Ag 3*d*<sub>5/2</sub> peak and Fermi edge of clean polycrystalline Ag prior to the start of the experiments, with the transmission function determined using various clean metallic foils. The binding energies of the data were adjusted during the analysis, using the C-C/C-H component in the C 1s region at 285.0 eV as the reference point.

# 2. Supplementary Figures



**Figure S1**: The images of 0.1wt% NZeo electrolyte suspension. a). after ultrasonic treatment for 2min; b, c). after ultrasonic treatment and rested for 24h.

The ZSM-5 zeolite we used in this work (NanoH-ZSM-5 P91) was purchased from ACS Material. It has a molar ratio of SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub> of 91, crystallite size of 300 nm, BET 362 m<sup>2</sup>/g, and a pore size of ~5Å. To prepare a homogeneous suspension with ZSM-5 in electrolyte, we used ultrasonic treatment for 2 min before assembling the cell. The images of the suspension after ultrasonic treatment and then rested for 24h are presented in Figure S1 a-c. A homogeneous suspension is obtained after sonication as shown in Figure S1a, while the NZeo particles precipitated during resting can be observed in Figure S1b and S1c.



**Fig. S2**: Electrochemical performance of  $Na_aMO_2/C$  full cells using different electrolyte additives. a). The capacity retention during cycling at 0.8 C after formation. b). Comparison of the specific capacity of the 1<sup>st</sup> and 50<sup>th</sup> cycle for each electrolyte type.

Following coin cell assembly, all cells were subjected to formation cycles where a small current at 10 mA/g (0.12 mA/cm<sup>2</sup>) was applied to generate a SEI layer between 1.0 - 4.2 V. Similar initial charge capacities normalised for the cathode weight of approximately 150 mAh/g, and first discharge capacities of ~130 mAh/g were observed for all cells containing the different electrolyte additives, as is expected for these cathode materials. This confirms we are achieving the full capacity of these materials in this cell set-up.



**Fig. S3**: a. Electrochemical performance of the full cells assembled with 3-electrodes Swagelok cell. Red, blue and green curves represent the voltage profile of working electrodes, counter electrodes and the full cells; b. Differential capacity *vs*. counter electrode potential in 3-electrode Swagelok full cells systems. Grey and orange curves represent the  $1^{st}$  and  $2^{nd}$  cycle.

Three-electrode cells were assembled to locate the plateaus in the full cell that are presented in **Fig. S3** to investigate the voltage profiles of the working and counter electrodes independently in the full cell configuration. In a three-electrode cell system, metallic Na is the reference electrode,  $Na_aMO_2$  and hard carbon are the working electrode (WE) and counter electrode (CE) respectively. The three-electrode full cells were assembled with Std, FEC and NZeo electrolytes. The voltage profile of WE (red curves) and CE (blue curves) are recorded simultaneously as shown in Fig. S3a. The voltage curves of the cell are also presented as green curves in the figure. As discussed previously, the peak around 2.2 V is only observed in the full cell assembled with FEC electrolyte. The voltage at which decomposition occurs is marked in the full cell charging profile and mapped correspondingly on the working and counter electrode charging profiles. From comparison, the peak can be located to the plateau around 650 mV vs. Na<sup>+</sup>/Na observed in the counter electrode charging profile in the FEC electrolyte, corresponding to the peak at ~650 mV in the differential capacity plot (Fig. S3b). The peak is no longer detected in the second cycle as shown in the differential capacity plots and which is also verified in the derivative curves in the full cell in Fig. 1. This confirms that the different charging voltage profile for the full cell is caused by the reduction of FEC on the hard carbon and indicates that the reduction is likely completed after the first cycle.



**Fig S4.** Photographs of the dissembled cell components and SEM images of the non-plating regions of the anode coating for Std (a, a') FEC (b, b') and NZeo (c, c') electrolytes after 480 cycles at 100 mA/g.



**Fig S5**. (a) Photographs of the dissembled cell components and (b) the cycle life comparison for 1wt% and 0.1wt% NZeo content respectively after 480 cycles at 100 mA/g.



**Fig. S6.** Elemental dispersive spectroscopy maps of the negative electrode surface with the presence of NZeo.

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