Supporting Information

# Surfactant opens the electrochemical window of aqueous electrolyte for better rechargeable aqueous Sodium/Zinc battery

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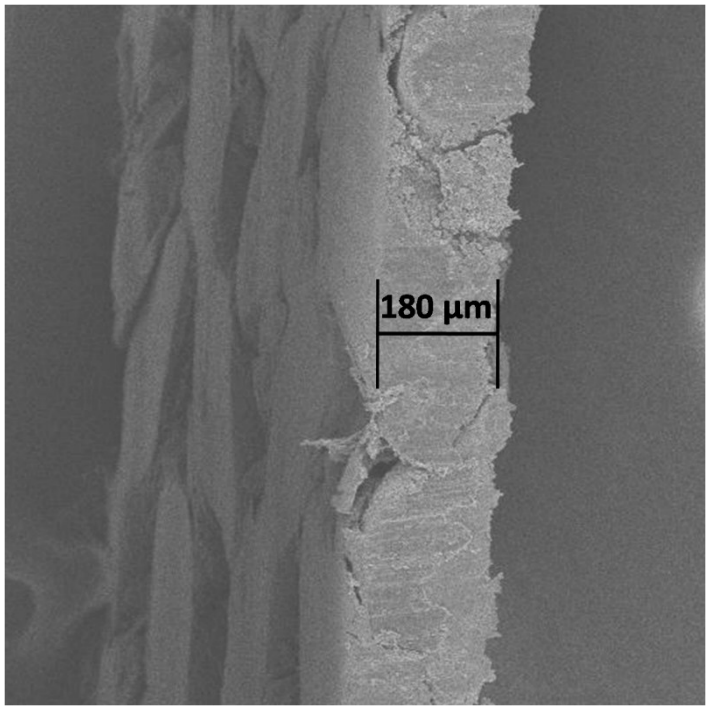


**Figure S1**. The SEM image of as-prepared cathode electrode. The thickness of the cathode electrode is about 180 µm.

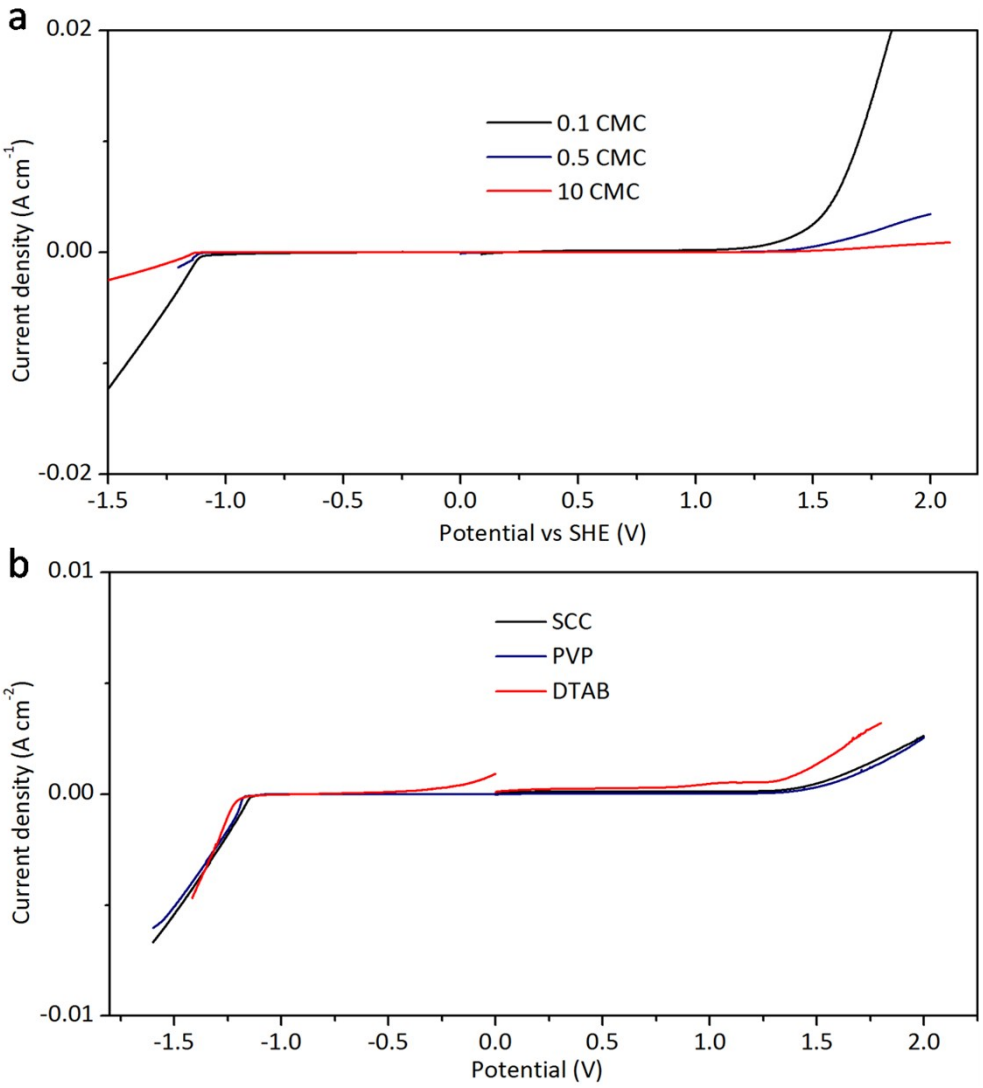


**Figure S2**. Electrochemical stable window of different electrolyte measurements were taken with linear sweep voltammetry on titanium slice electrodes versus Ag/AgCl at 10 mV $s^{-1}$, whereas the potential has been converted to standard hydrogen electrode (SHE) reference. (a) Electrochemical stable window of electrolyte with different SDS concentrations. 0.1 CMC represents about 0.0008 mol $L^{-1}$ SDS. 10 CMC is about 0.08 mol $L^{-1}$ SDS in the electrolyte. (b) Electrochemical stable window of electrolyte with different surfactant in their own critical micelle concentration, respectively.

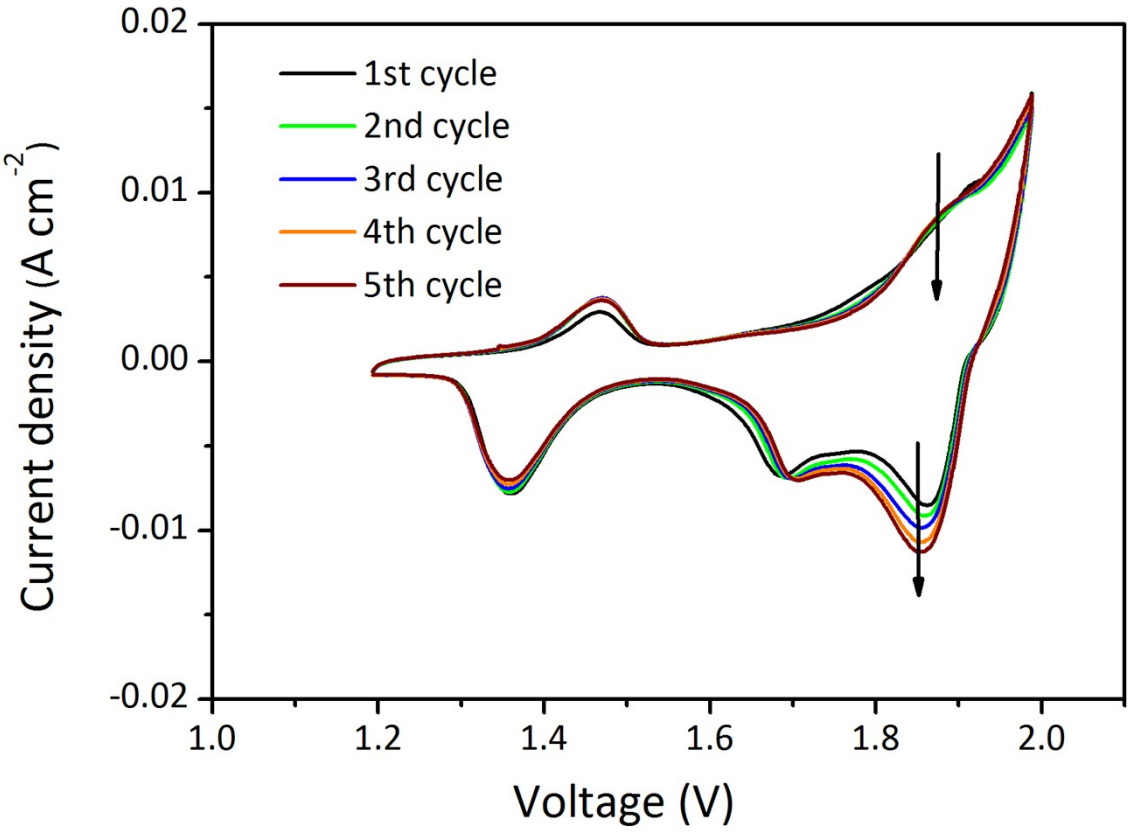


**Fig. S3.** CV profiles of the full battery in SDS added electrolyte at a scan rate of 5 mV $s^{-1}$ in a voltage range between 1.2 V and 2 V.

| Electrode couples | Operating voltage (V) | Cycle performance | Energy density (W h/kg) | References |
|---|---|---|---|---|
| **$LiMn_2O_4$/ $VO_2$** | 1.5 | 100 (80%) | 55 | S1 |
| **$Na_{0.44}MnO_2$/$NaTi_2(PO_4)_3$** | 1.1 | 1600 (50%) | 50 | S2 |
| **$Na_{0.95}MnO_2$/zinc** | 1.5 | 1000 (100%) | 35 | S3 |
| **Copperhexacyanoferrate/ manganesehexacyanomanganate** | 1.0 | 1000 (100%) | 25 | S4 |
| **$Na_{0.66}Mn_{0.66}Ti_{0.34}O2$/$NaTi_2(PO_4)_3$** | 1.2 | 300 (75%) | 60 | S5 |
| **$Na_3V_2(PO_4)_3$/zinc** | 1.4 | 200 (60%) | 100 | S6 |
| **Indium hexacyanoferrate/ $NaTi_2(PO_4)_3$** | 1.6 | 200 (90%) | 36 | S7 |
| **$Na_2MnFe(CN)_6$/zinc** | 1.7 | 2000 (75%) | 170 | This work |

**Table S1**. The electrochemical performance of various electrodes in aqueous electrolyte cells.

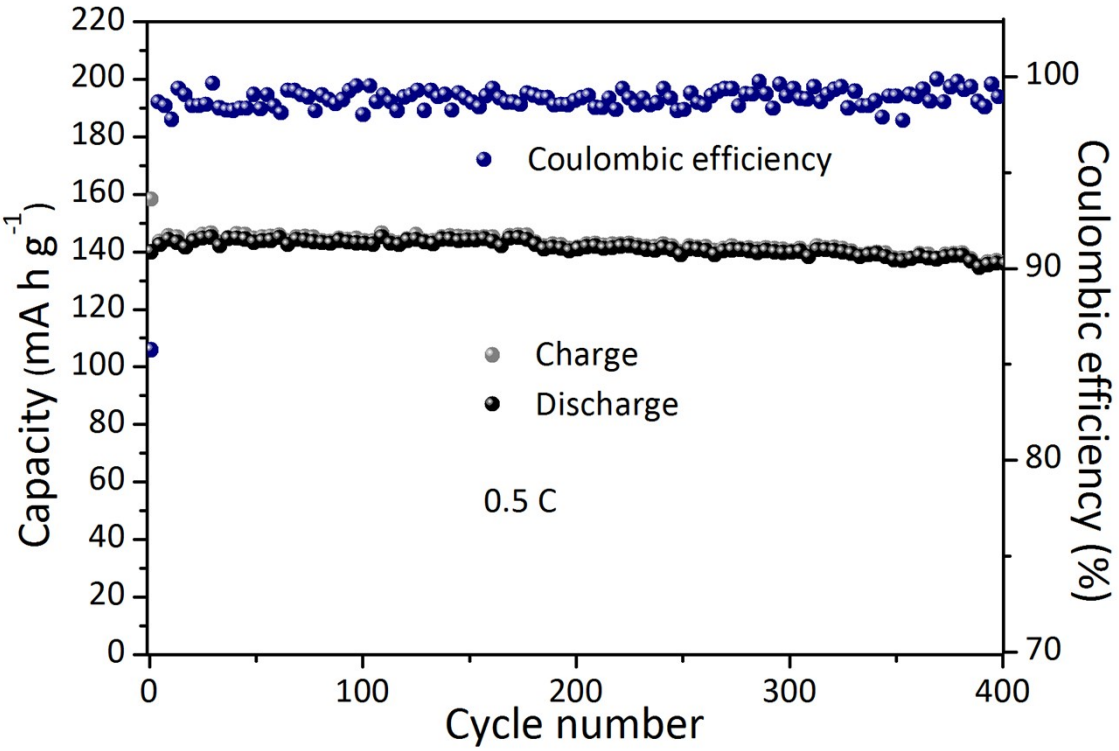


**Figure S4**. Cycle performance of the full cell at a rate of 0.5 C.

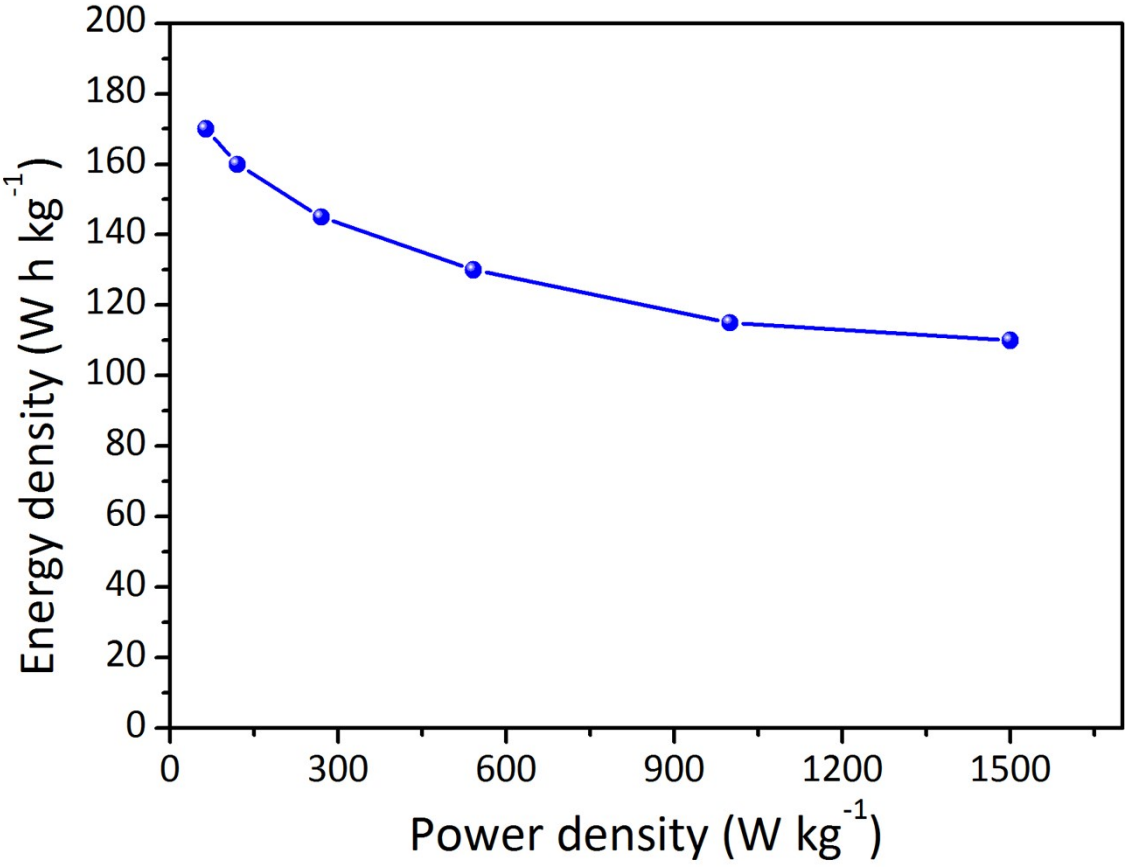


**Figure S5**. Ragone plot of the aqueous rechargeable sodium/zinc battery.

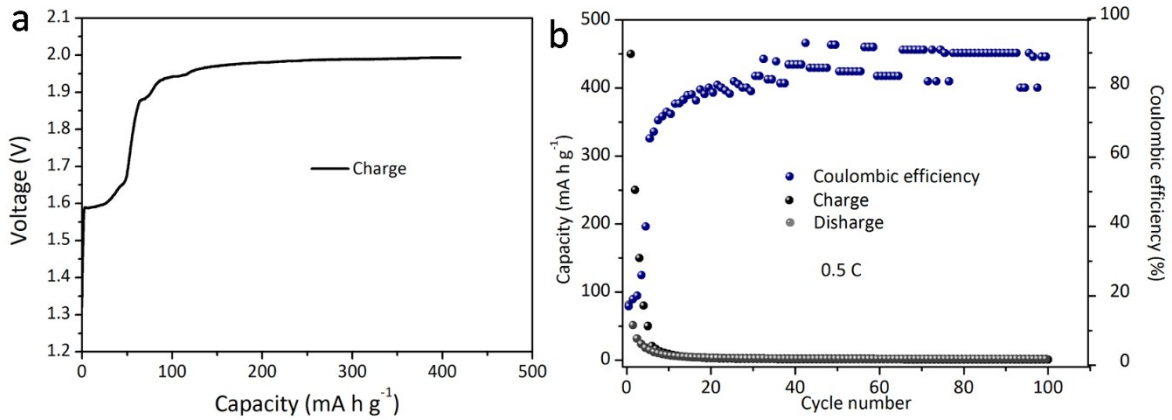


**Figure S6**. (a)Typical charge profile of the $Na_2MnFe(CN_6)$/zinc battery at a rate of 0.5 C in a voltage range from 1 V to 2 V using pristine electrolyte. (b) Cycle performance of the full cell in pristine electrolyte at 0.5 C.

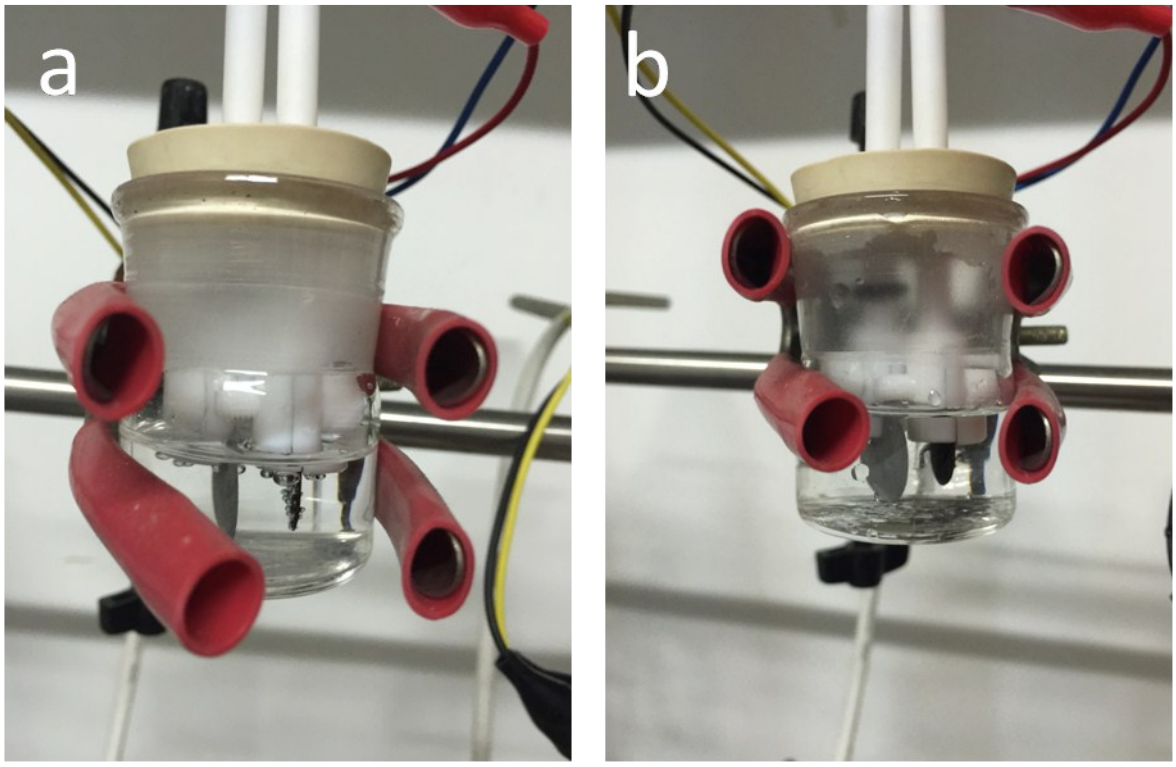


**Figure S7**. Photograph of the as-assembled full cell using pristine electrolyte and SDS added electrolyte respectively. The battery was charged to 2.0 V at 0.5 C. The electrode on the left is zinc anode and the electrode on the right is cathode. The electrode holders are made by platinum sheets which are inlaid into plastic to hold the electrode. The bottles are made by glass and sealed with rubber plug.

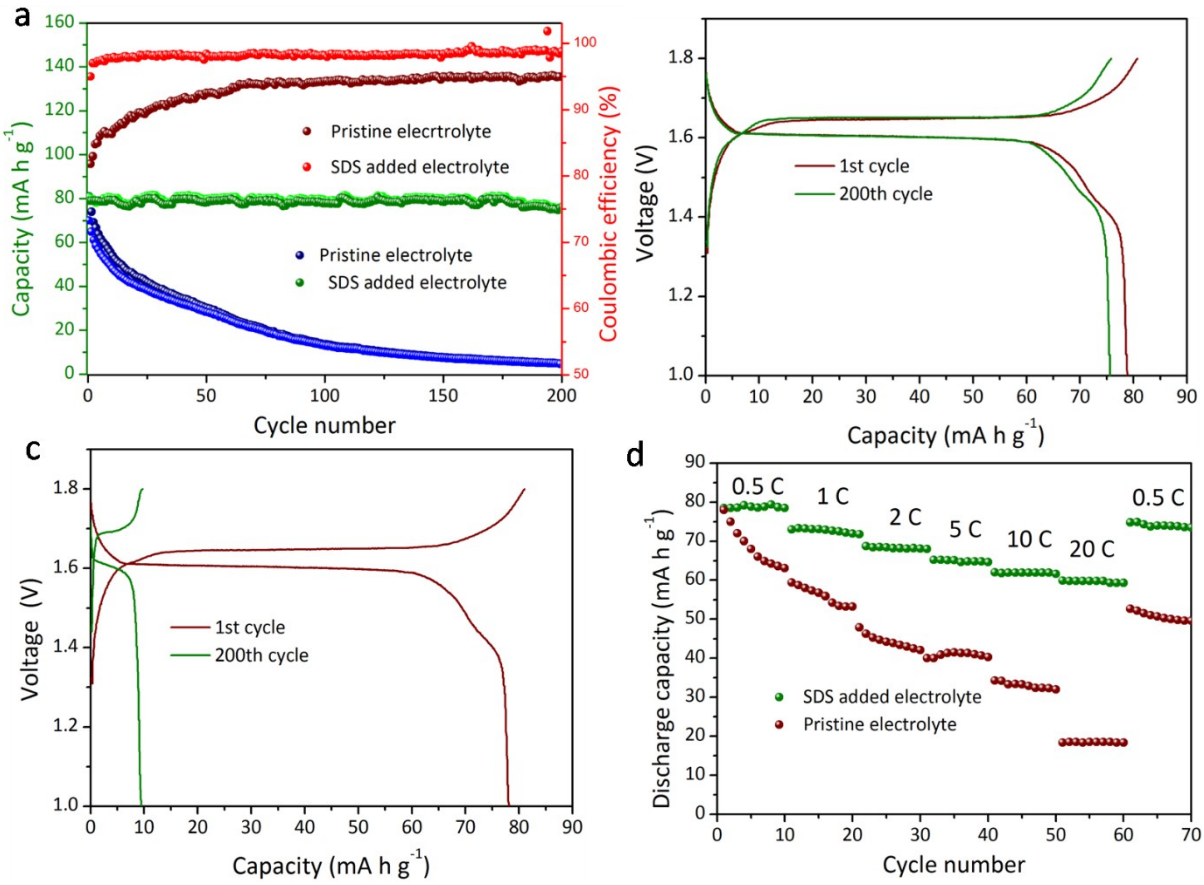


**Fig. S8.** (a) Cycle stability tests of full cell in pristine electrolyte and SDS added electrolyte in a voltage range of 1.0-1.8 V at 0.5 C (1 C =160 mA $g^{-1}$, 0. 5 C = 80 mA $g^{-1}$), respectively. (b) Charge/discharge profiles at a rate of 0.5 C in SDS added electrolyte. (c) Charge/discharge profiles at 0.5 C in pristine electrolyte. (d) Rate capability of the battery of full cell in pristine electrolyte and SDS added electrolyte in a voltage range of 1.0-1.8 V, respectively.

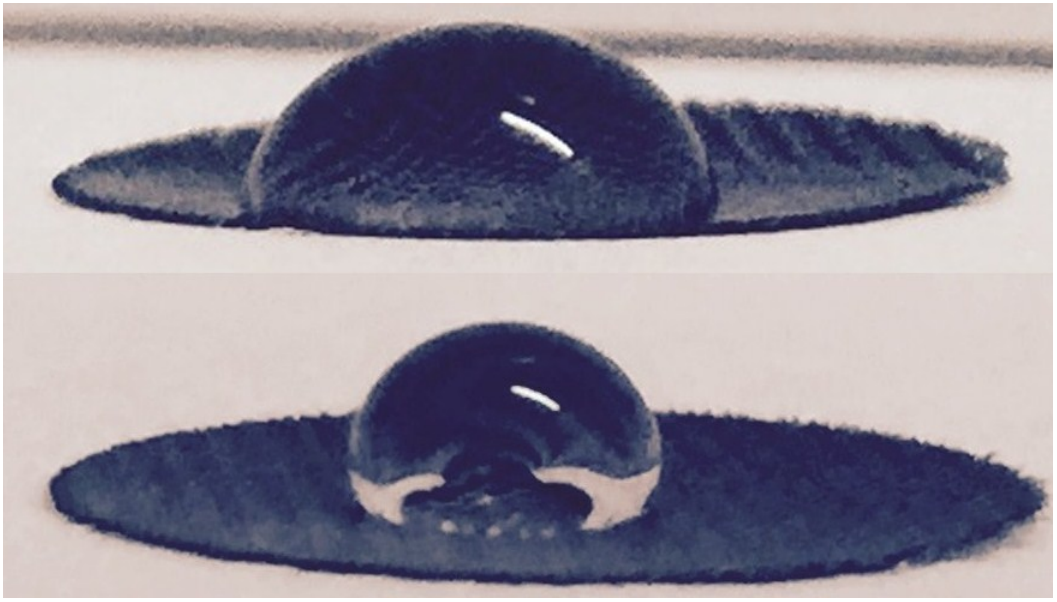

**Fig. S9.** Wetting angles of pristine electrolyte (upper) and SDS added electrolyte (below) droplet on cathode electrodes, respectively.

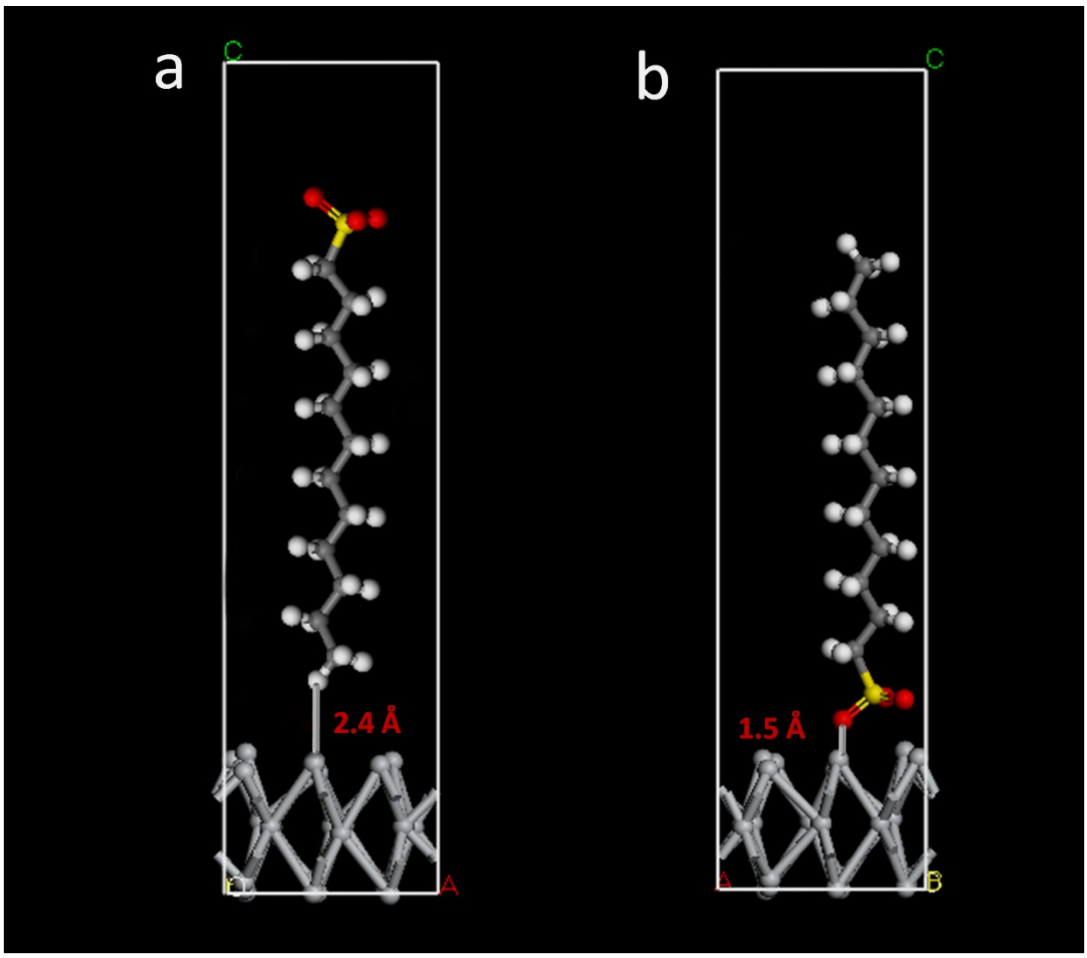


**Fig. S10.** The models of DFT calculation show the interactions between Ti and SDS molecule hydrophobic tail (a), and SDS molecule hydrophilic group with Ti (b). The carbon (C), sulphur (S), tintanium (Ti), hydrogen (H) and oxygen (O) atoms are denoted by dark gray, yellow, celadon, white and red spheres respectively.

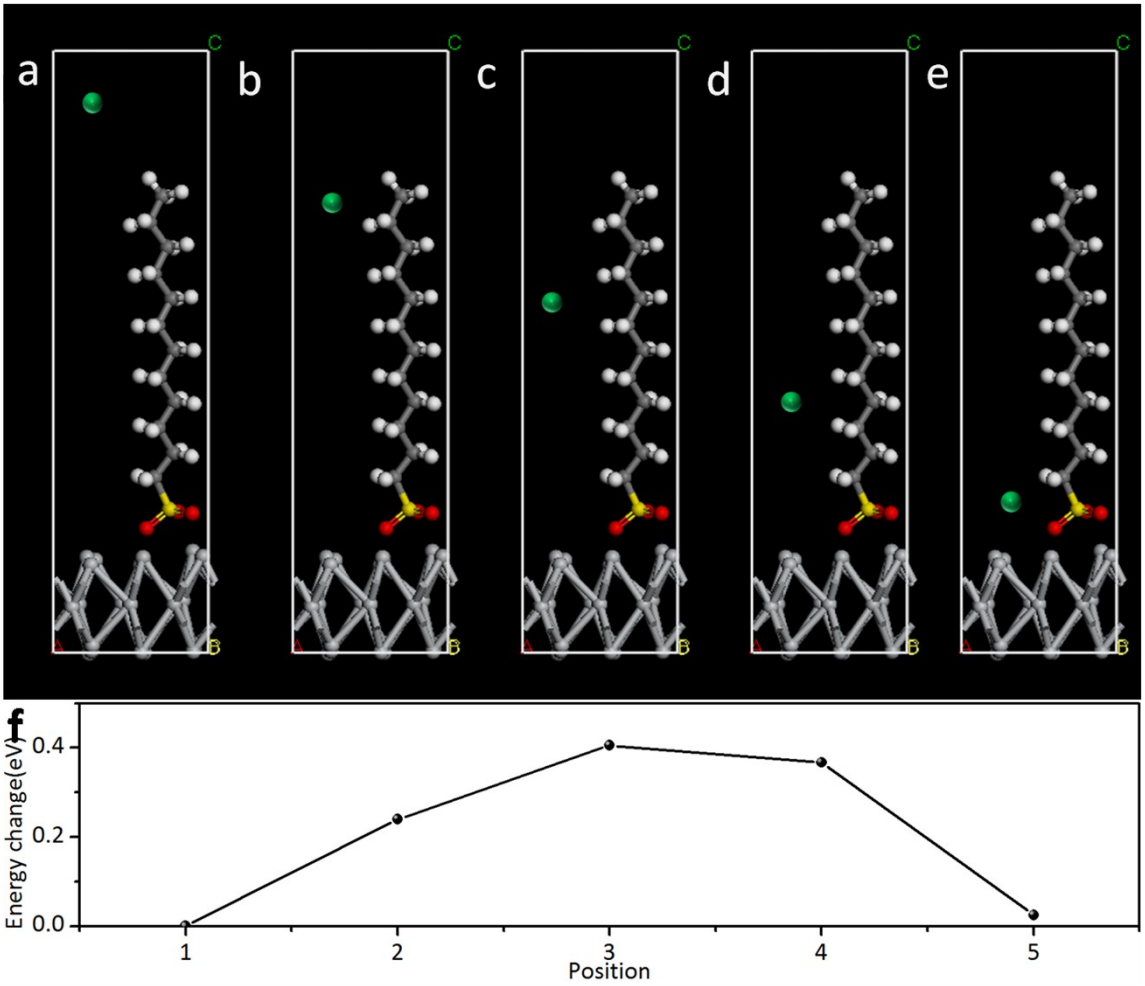


**Fig. S11.** The models of density functional theory calculation, showing the sodium ion goes through SDS adsorption interlayer at different stations (a, b, c, d and e). (f) The tendency of energy change at different situations. The carbon (C), sulphur (S), tintanium (Ti), hydrogen (H), oxygen (O) atoms and sodium (Na) ion are denoted by dark gray, yellow, celadon, white, red and green spheres respectively.

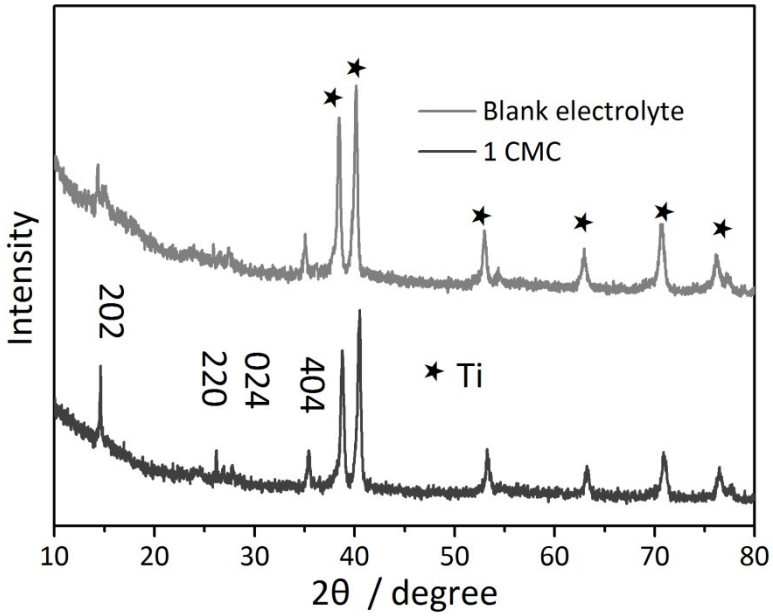


**Figure S12**. X-ray diffraction patterns of cathode electrodes after 100 cycles in different electrolyte (peaks labeled with black stars corresponding to Ti mesh current collector).

| electrolyte | Mn concentration (ug $mL^{-1}$) | mass fraction (wt.%) |
|---|---|---|
| pristine electrolyte | 10.0 | 66.0 |
| SDS added electrolyte | 0.03 | 0.2 |

**Table S2**. Inductive Coupled Plasma Emission Spectrometer-Atomic Emission Spectroscopy (ICP-AES) analysis of Mn in different electrolyte at a voltage range between 1.0 and 2.0 V after 2000 cycles.

| electrolyte | Mn concentration (ug $mL^{-1}$) |
|---|---|
| pristine electrolyte | 9.50 |
| SDS added electrolyte | 0.02 |

**Table S3.** (ICP-AES) analysis of Mn in different electrolyte at a voltage range between 1.0 and 1.8 V after 200 cycles.

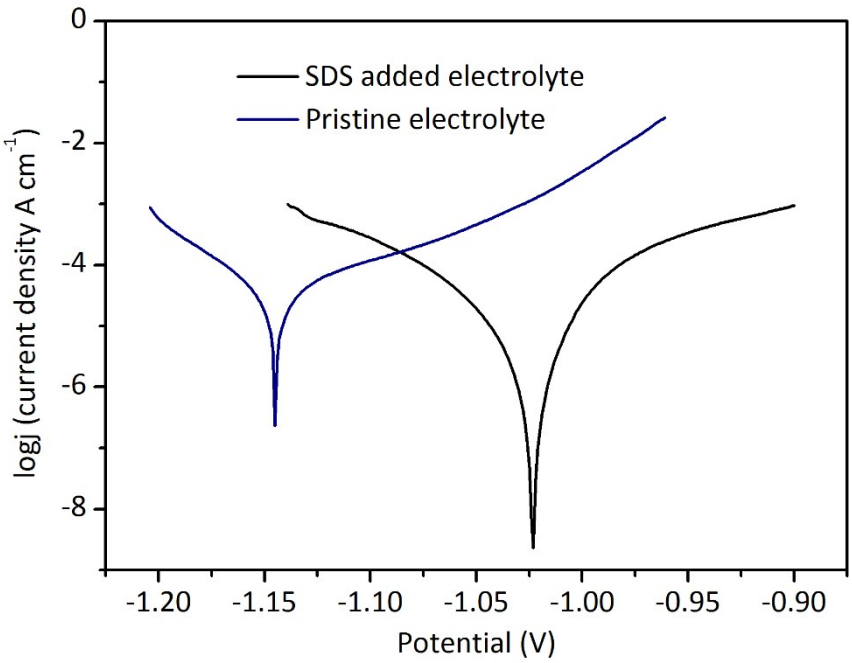


**Figure S13**. Polarization curves of Zn in different electrolyte at a scan rate of 10 mV $s^{-1}$.

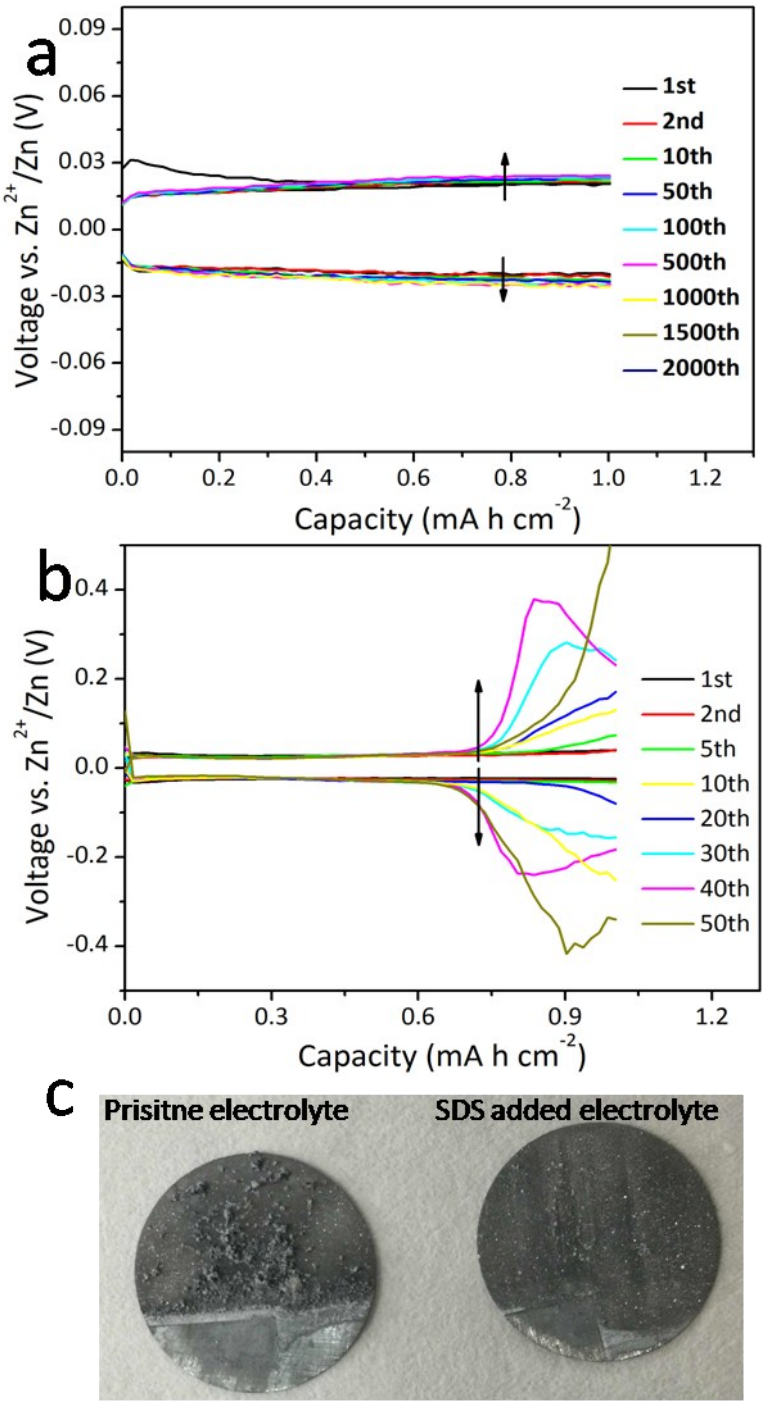


**Fig. S14.** Voltage profiles of Zn plating/stripping in the SDS added electrolyte (a) and pristine electrolyte (b) at a current density of 1 mA $cm^{-2}$ on the Zn sheet and the plating/stripping of Zn was controlled by the capacity (1 mA h). (c) Photograph of the Zn anode after 100 plating/stripping tests.

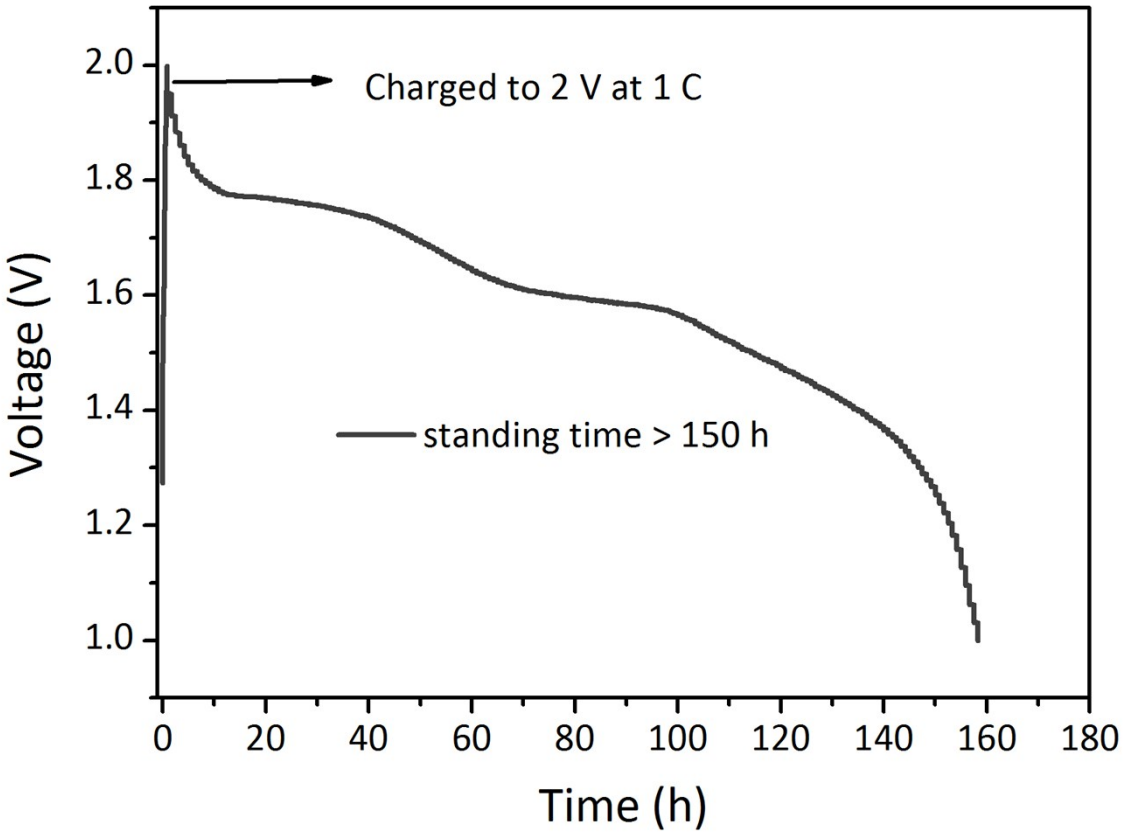


**Figure S15**. Self-discharge tests of full cell in SDS added electrolyte.

**References**

S1. Li, W., Dahn, J. & Wainwright, D. Rechargeable lithium batteries with aqueous electrolytes. *Science* **264**, 1115-1118 (1994).

S2. Li, Z., Young, D., Xiang, K., Carter, W. C. & Chiang, Y. M. Towards High Power High Energy Aqueous Sodium-Ion Batteries: The $NaTi_2(PO_4)_3/Na_{0.44}MnO_2$ System. *Adv. Energy Mater.* **3**, 290-294 (2013).

S3. Zhang, B. *et al.* An aqueous rechargeable battery based on zinc anode and $Na_{0.95}MnO_2$. *Chem. Commun.* **50**, 1209-1211 (2014).

S4. Pasta, M. *et al.* Full open-framework batteries for stationary energy storage. *Nat. Commun.* **5**, 3007-3015 (2014).

S5. Wang, Y. *et al.* A Novel High Capacity Positive Electrode Material with Tunnel-Type Structure for Aqueous Sodium-Ion Batteries. *Adv. Energy Mater.* **5**, 1501005-1501014 (2015).

S6. Li, G., Yang, Z., Jiang, Y., Zhang, W. & Huang, Y. Hybrid aqueous battery based on $Na_3V_2(PO_4)_3$/C cathode and zinc anode for potential large-scale energy storage. *J. Power Sources* **308**, 52-57 (2016).

S7. Pan, H. *et al.* Reversible aqueous zinc/manganese oxide energy storage from conversion reactions. *Nat. Energy* **1**, 16039-16045 (2016).