## Reconfiguring the helmholtz plane with a trace polar additive for highly reversible Zinc anodes

Yu Lu, Yanxin Wang, Chenyang Guo, Mingyue Chen, Kunyu Hao, Pengcheng Qi, Yiwen

Tang\*

Institute of Nano-Science and Technology, College of Physical Science and Technology, Central China Normal University, Wuhan, 430079, China

\*Corresponding author: <u>Tel: +86-27-67867947</u>; Fax: +86-27-67861185; e-mail:\_ <u>ywtang@ccnu.edu.cn</u>



Fig. S1. Adsorption modes of  $H_2O$  and TAA on Zn (002) surface and the corresponding

adsorption energy.



Fig. S2. The XRD pattern of zinc electrodes after immersion in 2 M  $ZnSO_4$  and 2 M  $ZnSO_4$  with 10 mM TAA electrolytes.



Fig. S3. The SEM images of zinc electrodes after immersion in (a) 2 M ZnSO<sub>4</sub> and (b)  $2 M ZnSO_4 + 10 mM$  TAA electrolytes.



Fig. S4. The obtained EDL capacitances in in different electrolytes with/without TAA. Electric double layer capacitance measurements of Zn substrates in two electrolytes (b) 2 M ZnSO<sub>4</sub> and (c) 2 M ZnSO<sub>4</sub> +10 mM TAA. Cyclic voltammograms of Zn-Zn symmetric coin cells recorded within a voltage range of -15 mV to 15 mV under

different scanning rates.



Fig. S5. EIS plots and CA of Zn||Zn symmetric cells in (a) 2 M ZnSO<sub>4</sub> (b) 2 M ZnSO<sub>4</sub>
+ 10 mM TAA electrolytes before and after polarization.

The transference number of Zn<sup>2+</sup> ( ${}^{t}_{Zn^{2}+}$ ) was calculated by the following equation:  $t_{Zn^{2}+} = \frac{I_{s}(\Delta V - I_{0}R_{0})}{I_{0}(\Delta V - I_{s}R_{s})}$ 

Where  $\Delta V$  is the applied voltage (20 mV);  $I_0$  and  $R_0$  are the initial current and resistances, respectively; and  $I_s$  and  $R_s$  are the steady-state current and resistance, respectively.



Fig. S6. FTIR amplified spectra of ZnSO<sub>4</sub> electrolytes with/without TAA.



Fig. S7. (a) Snapshot of the MS simulation cells for TAA-based electrolyte. (b) The radial distribution functions of  $Zn^{2+}$ -O (H<sub>2</sub>O) and  $Zn^{2+}$ -S (TAA). (c) The coordination numbers of  $Zn^{2+}$ -O (H<sub>2</sub>O) in TAA-based electrolyte.



Fig. S8. Comparison of XRD images for the zinc anode after various cycles in (a) 2 M  $ZnSO_4$  and (b) 2 M  $ZnSO_4 + 10$  mM TAA electrolytes.



Fig. S9. The high-magnification SEM images of zinc anode after different cycles in 2 M  $ZnSO_4$ +10 mM TAA electrolyte at a current density of 1 mA cm<sup>-2</sup>.



Fig. S10 (a) EIS curves. (b) ionic conductivity of  $ZnSO_4$  electrolyte and  $ZnSO_4$  electrolyte with various contents of additive.



Fig. S11. Cycling stability of Zn||Zn symmetric cells in different electrolytes (a) ZnSO<sub>4</sub> + 5 mM TAA. (b) ZnSO<sub>4</sub> + 20 mM TAA.



Fig. S12. The rate performance of Zn||Zn symmetric cells in  $ZnSO_4 + 10$  mM TAA.



Fig. S13. Nyquist patterns of the Zn||Zn symmetric cells in different electrolytes (a) ZnSO<sub>4</sub>. (b) ZnSO<sub>4</sub> + 10 mM TAA at various temperatures.

The active energy ( $E_{a}$ ) could be calculated based on Arrhenius Equation:

$$R_{ct}^{-1} = Aexp(-\frac{E_a}{RT})$$

where  $R_{ct}$  is the charge transfer resistance, A is the frequency factor, R is the gas constant, and T is the absolute temperature.



Fig. S14. The XRD image of V<sub>6</sub>O<sub>13</sub> powder.



Fig. S15. The SEM image of  $V_6O_{13}$  powder.