Electronic Supplementary Information

$ZnCl_2$ Water-in-Salt Electrolyte for Reversible of Zn Metal Anode

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EXPERIMENTAL PROCEDURES

Materials

$ZnCl_2$, and Zinc foil (0.1 mm thick, 99.5%) were purchased from Acros Organics and Alfa Aesar. Glass fiber (GF/D borosilicate) was purchased from Whatman. Carbon paper was purchased from FuelCellStore.

Electrolyte characterization

FTIR spectra were carried out on a NICOLET 5397 AVATAR 360 FTIR. SEM images were collected on FEI NOVA 230 high-resolution scanning electron microscopy. Femtosecond stimulated Raman spectroscopy (FSRS) measurements were performed according to the previously reported method.[1] The measurement of transference number for the dilute and concentrated $ZnCl_2$ electrolytes followed the reported method.[2]

Electrochemical measurements

The electrochemical stability window of the $ZnCl_2$ electrolytes. Linear sweep voltammetry was carried out on titanium foil in a three-electrode cell with Ag/AgCl (saturated KCl solution, 0.198 V vs standard hydrogen electrode) as a reference electrode and free-standing activated carbon film as the counter electrode at a scan rate of 0.2 mV s^{-1}. The activated carbon counter electrode was prepared by mixing 80% activated carbon, 10% super P conducting carbon, and 10% polytetrafluoroethylene (PTFE).

The measurements of Zn plating/striping. The symmetric cells were assembled in two-electrode coin cells by using both Zn foil (0.25 cm^2) as the anode and cathode with a glass-fiber separator. In asymmetric Zn||Zn cells, the process of CE measurements followed the reported method.[3] Briefly, Ti foil was first preconditioned with one cycle at a capacity of 4 mAh cm^{-2} to eliminate the oxidants of the substrate surface. Then a given amount of charge (Q_T, 4 mAh cm^{-2}) was employed to deposit Zn on Ti foil. Next, a smaller capacity (Q_C, 0.4 mAh cm^{-2}) was used to cycle between the Ti foil working electrode and the Zn counter electrode for 100 cycles. Finally, the remaining of the Zn reservoir was exhaustively stripped to the cut-off potential, obtaining the final stripping charge capacity of Q_S. Thus, the average CE can be calculated by:

$$CE = \frac{100 * Q_c + Q_s}{100 * Q_c + Q_T}$$

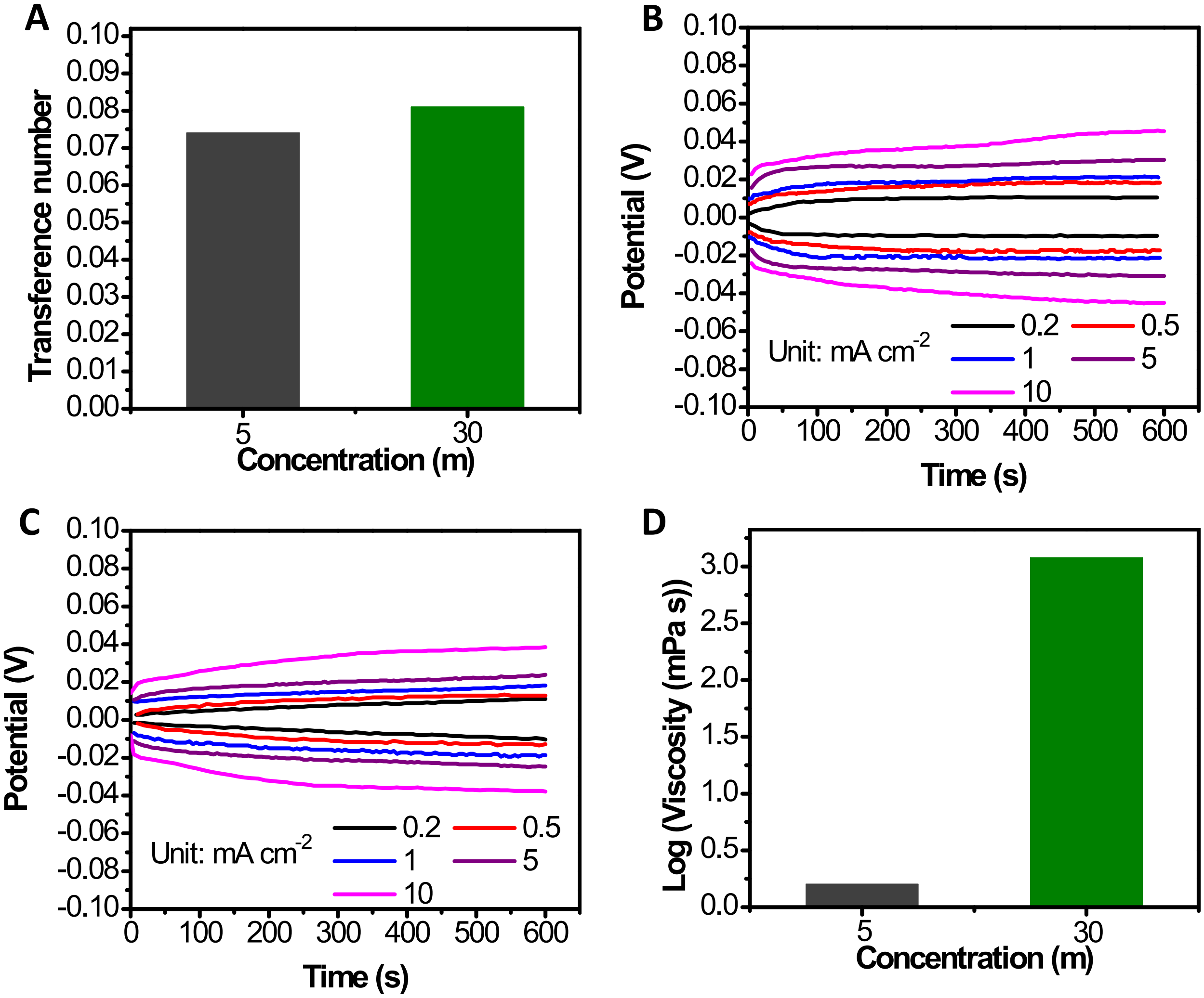

Figure S1. (A) The transference number of Zn^{2+} at 21 ^{o}C for dilute (5 m) and concentrated (30 m) $ZnCl_2$ electrolytes. GCD curves for Zn anode in (B) 5 m and (C) 30 m $ZnCl_2$ electrolyte in symmetric cells. (D) The viscosity at 21 ^{o}C for dilute (5 m) and concentrated (30 m) $ZnCl_2$ electrolytes.

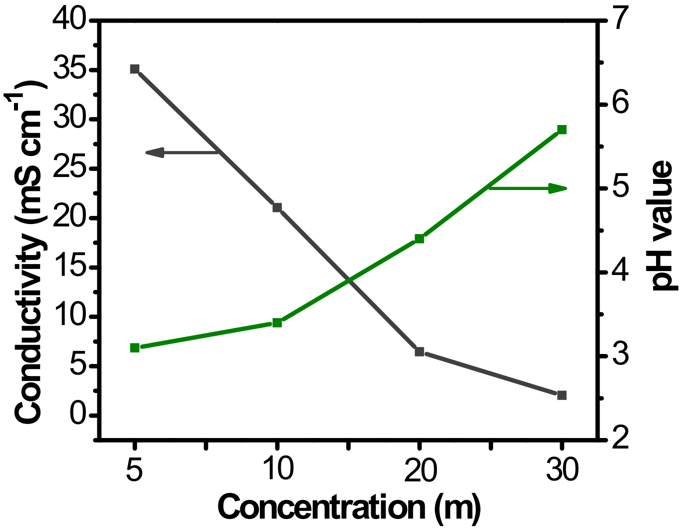

Figure S2. The conductivity and pH values for the $ZnCl_2$ electrolytes with different concentrations.

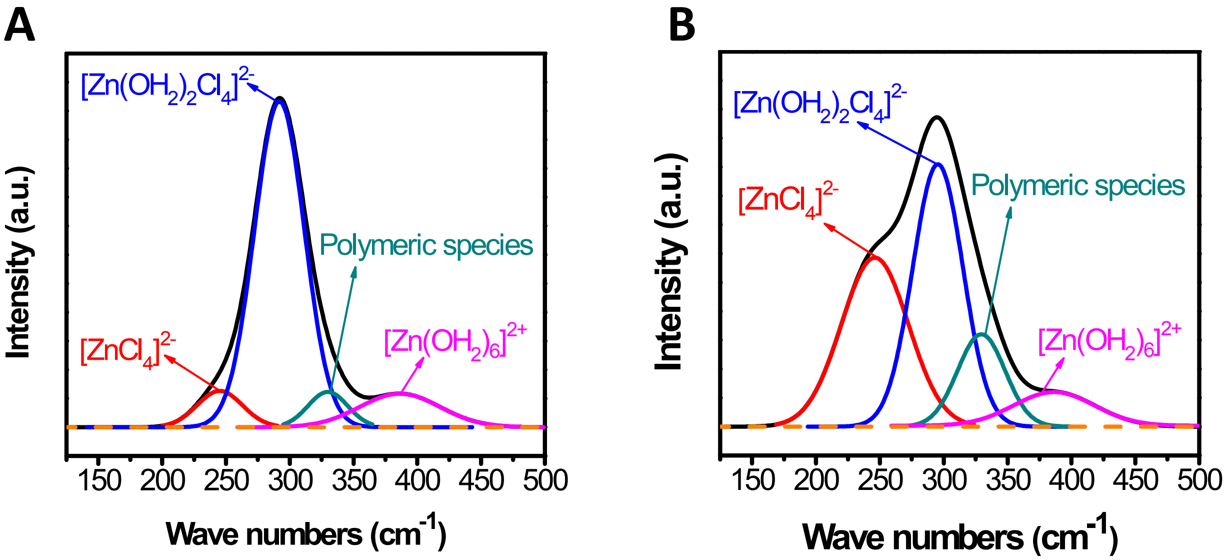

Figure S3. Raman spectra of $ZnCl_2$ electrolytes with the concentrations of (A) 20 m and (B) 30 m.

With the deconvolution of Raman spectra, the peak intensity of $[Zn(OH_2)_6]^{2+}$ in the 20 m $ZnCl_2$ electrolyte is similar to that in the 30 m $ZnCl_2$ electrolyte, where the ratio of peak intensity between 20 m and 30 m $ZnCl_2$ is 1:1.08. However, the ratio of peak intensity for the anions ($[Zn(OH_2)_2Cl_4]^{2-}$ + $[ZnCl_4]^{2-}$) between the 20 m and 30 m $ZnCl_2$ electrolytes is 1.36 : 1.

References

1 L. Zhu, Liu, W. Liu and C. Fang, *Appl. Phys. Lett.,* 2015, **105**, 041106.

2 P. G. Bruce and C. A. Vincent, *J. Electroanal. Chem. Interfacial Electroem.*, 1987, **225**, 1.

3 B. D. Aadamas, J. Zheng, X. Ren, W. Xu and J.-G. Zhang, *Adv. Energy Mater.,* 2015, **8**, 1702097.