



Amide-based molten electrolyte with hybrid active ions for rechargeable Zn batteries

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ABSTRACT

Rechargeable Zn batteries (ZBs) have received increasing attention due to their cheap, safe and green characteristics, but their further development is generally bottlenecked by lack of compatible electrolytes. Here we report an eco-friendly and low-cost amide-based molten salt (AMS) containing acetamide, lithium bis(trifluoromethane sulfonyl) imide (LiTFSI) and trifluoromethylsulfonate (Zn(Tfo)₂) for ZBs. This AMS electrolyte enables a ~100% Zn plating/stripping efficiency with long-term stability and suppresses Zn dendrite growth. Based on the Li⁺ extraction/insertion on the cathodes and reversible Zn chemistry on the anode in this AMS electrolyte, both Zn/LiMn₂O₄ and Zn/LiFePO₄ batteries show excellent electrochemical performance including large specific capacity (118 and 140 mAh g⁻¹, respectively) and remarkable cycle life (>150 cycles). More importantly, by virtue of the electrochemical stability of the AMS, the voltage limit can be significantly increased above 2.15 V for the Zn/LiMn₂O₄ battery, making full use of the cathode capacity. This finding opens new opportunities for the development of low-cost and high performance ZBs.

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1. Introduction

Although lithium-ion batteries (LIBs) have been widely used in portable electronics and are recognized as the best choice for electric vehicles, the increasing cost and limited resources of lithium may restrict their scale-up applications [1,2]. Zn batteries (ZBs), which are one of the most mature battery systems and characterized by low cost and abundant supply of raw materials, show great potential for facilitating large-scale deployment of renewable electricity generation sources [3–7]. Several new types of ZBs based on Zn²⁺ ion (de)intercalated cathodes such as MnO₂, V₂O₅, LiV₃O₈ and hexacyanoferrate have been proposed recently, and the intercalation mechanism was also fully investigated [8–15]. But so far there are still many problems concerning Zn anode in the presence of aqueous electrolytes, like dendrite formation,

passivation and H₂ evolution, which significantly limit cyclability and further commercialization [16–18].

Searching for alternative electrolytes to overcome the above issues is necessary for promoting ZBs as practical cost-effective energy storage systems [19–21]. Ionic liquids (ILs), owing to good electrical conductivity, high stability and large electrochemical window, have been investigated as potential electrolytes for wide electrochemical applications [22,23]. Researchers have demonstrated the electrodeposition of Zn from ILs, which is strongly dependent on the structure and composition of the ILs [24]. However, common ILs, typically containing organic cations and anions, are generally sensitive to water and have exorbitant prices [25]. The amide-based molten salts (AMS) offer a viable and green alternative choice due to their comparable electrochemical and physical properties with easy availability and good water compatibility, which have been successfully used in LIBs [26]. Along this line, ZBs using AMS as their electrolytes could be more cost-effective and function significantly longer. However, the performance of the AMS remains imperfect and critical knowledge is still missing for adjusting composition and ratio suitable for various energy storage devices.

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In the present paper, we report room-temperature AMS electrolytes composed of acetamide, LiTFSI, and $\text{Zn}(\text{Tfo})_2$, and study their application in secondary ZBs. Compared with common aqueous electrolytes, such AMS electrolytes combine several important characteristics including high ionic conductivity (0.35 mS cm^{-1} at 30°C), low viscosity (0.29 Pa s), high electrochemical stability, and wide electrochemical window ($\sim 3.0 \text{ V}$). Moreover, a $\sim 100\%$ coulombic efficiency (CE) of Zn stripping/plating and suppressed Zn dendrite can be achieved in the AMS electrolyte. This study provides some insights for addressing the challenges faced in the practical use of the ZBs.

2. Experimental

2.1. Preparation of AMS electrolytes

Our strategy for seeking a room-temperature hydrate melt of Li salts consists of the careful selection of Li salt anions and the utilization of a eutectic system thereof. We select two organic imide anions, LiTFSI (Sigma-Aldrich Co.) and acetamide, whose melting points are 234°C and 81.2°C , respectively. The mechanical mixing of LiTFSI and acetamide with molar ratios between 1:3 and 1:4 and the addition of a small amount of $\text{Zn}(\text{Tfo})_2$ (Sigma-Aldrich Co.) (molar ratio: $\text{Li}^+/\text{Zn}^{2+} = 20$) lead to the formation of homogeneous liquid gradually at room temperature after stirring and storing overnight. This liquid can be also obtained immediately by heating the mixture at 80°C .

2.2. Sample characterization

The melting points of the electrolytes were determined with a DSC 2010 differential scanning calorimeter (TA Inc.) by sealing ca. 10 mg of the sample in an aluminum pan. The pan and the electrolyte were first cooled to about -80°C with liquid nitrogen and then heated to 100°C at a rate of $10^\circ\text{C}/\text{min}$. Raman spectra were recorded at the room temperature using a Thermo Scientific DXRxi system with a 532 nm laser. Fourier-transform infrared spectroscopy (FTIR) was recorded on a Bruker VECTOR 22 spectrometer in the frequency range of $4000\text{--}400 \text{ cm}^{-1}$. Morphological

information of the materials was obtained from field emission scanning electron microscopy (SEM, HITACHI S-4800).

2.3. Electrochemical measurement

The material preparation of FePO_4 is presented in the Supporting Information. XRD pattern of FePO_4 shows no signals of crystalline diffraction peaks, demonstrating an amorphous characteristic (Fig. S1). LiMn_2O_4 (LMO), LiFePO_4 (LFP) and V_2O_5 powders are obtained from Qingdao LNCM Co. Ltd., Shenzhen Dynanonic Co., Ltd and Energy Chemical, respectively, and no further treatment was performed. For the preparation of the cathode, the active material (LMO, LFP, FePO_4 or V_2O_5), Super P, and polyvinylidene fluoride (PVDF) binder were mixed thoroughly in a weight ratio of 70:20:10. And then the mixture was pasted on stainless steel (SS) sheet using a doctor blade and dried at 60°C for 24 h. As for the anode, Zn disks (purity of 99.9%) with a diameter of 14 mm was washed with ethanol and then pressed with a pressure of 20 MPa using a manual hydraulic press.

A conventional two electrode setup was used to perform the electrodeposition experiments. All of the electrodes were immersed in a unique compartment of a glass cell. SS was used as the working electrode (0.5 cm^2) and Zn metal as counter electrode. Chronopotentiometry (CP 200 μA , 1 h) was carried out on an electrochemical workstation.

Cyclic voltammetry (CV) was carried out on an electrochemical workstation (VMP-300, Bio-Logic Science Instruments Co.). For the three electrode setup, a saturated calomel electrode (SCE) and a Pt foil were employed as reference and counter electrodes, respectively. The electrochemical stability window of the electrolytes were measured on the inert current collector (SS). Galvanostatic charge/discharge measurements were performed with a LAND CT2001A Battery Cycler (Wuhan, China). The coin cells were assembled in air for Zn/LFP, Zn/LMO, Zn/ V_2O_5 , Zn/ FePO_4 batteries with AMS electrolyte and glass fiber separator.

3. Results and discussion

As shown in Fig. 1a, a homogenous and transparent liquid was

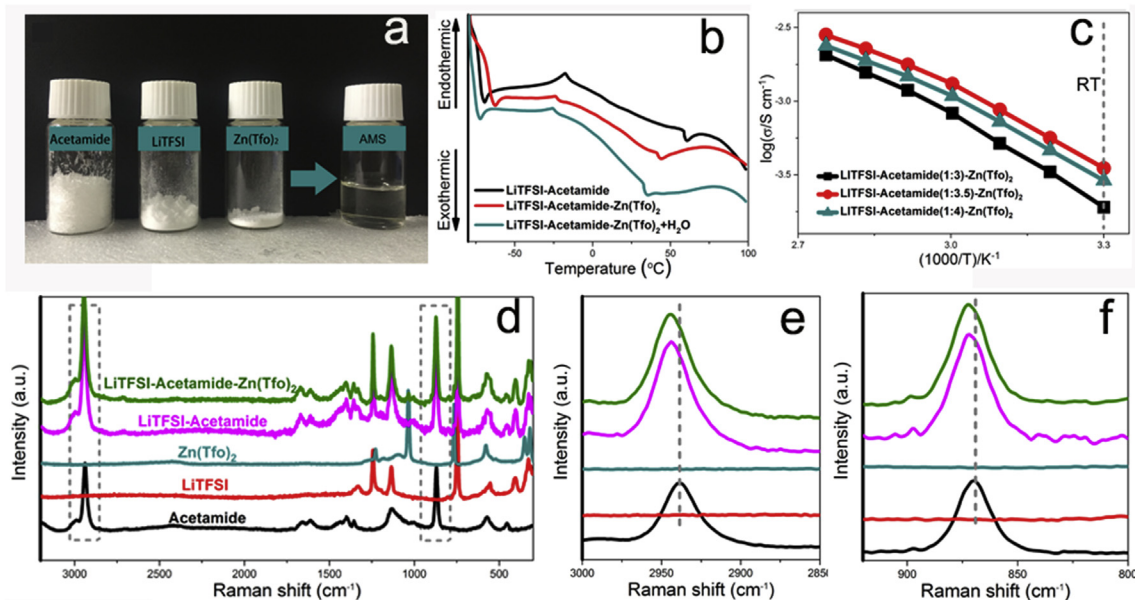


Fig. 1. (a) Using acetamide, LiTFSI and $\text{Zn}(\text{Tfo})_2$ to prepare AMS electrolyte. (b) DSC curves for the AMS. (c) Variation of ionic conductivity as a function of acetamide molar fraction in the AMS. (d) Raman spectra of AMS eutectic system (spectra of individual components including acetamide, LiTFSI and $\text{Zn}(\text{Tfo})_2$ are also given). (e, f) Selective enlargement of (d).

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