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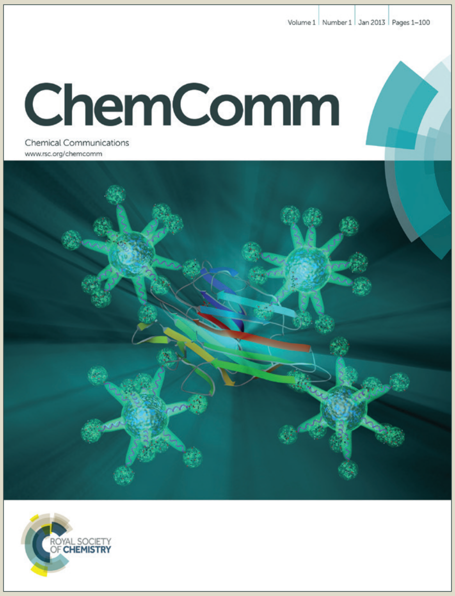

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High Performance Batteries Based on Hybrid Magnesium and Lithium Chemistry

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Yingwen Cheng, Yuyan Shao, Ji-Guang Zhang, Vincent L. Sprenkle, Jun Liu* and Guosheng Li*

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This work studied hybrid batteries assembled with Mg metal anode, a Li^+ ion intercalation cathode and a dual-salt electrolyte contains Mg^{2+} and Li^+ ions. We show that such hybrid batteries were able to combine the advantages of Li and Mg electrochemistry. They delivered outstanding rate performance (83% capacity retention at 15C) with superior safety and stability (~5% fade for 3000 cycles).

Advanced electrochemical energy storage systems are critical for the future as they could improve the efficiency of electric power grids, stimulate growth of renewable electricity generation, and provide alternatives to fossil fuels for transportation.[1] Because of these important characteristics, considerable effort has been devoted to developing batteries with higher energy density, improved safety and reliability, and reduced cost.[2, 3] Among the battery technologies, interest in rechargeable magnesium (Mg) batteries has increased because of their substantial prospective benefits.[4, 5] Mg metal is a low-cost, safe and environmentally benign material; when used as anode, Mg has a low standard electrode potential and fast deposition/stripping kinetics with nearly 100% reversibility without formation of dendritic structures.[6] Mg also has much higher theoretical energy density (gravimetric: 2205 mAh/g, volumetric: 3832 mAh/cm^3) compared with typical anode materials because of its divalent energy storage characteristics.[7] Over the past few years, substantial progress on rechargeable Mg batteries has been demonstrated, but their practical application is still facing great challenges, largely due to limitations of cathode materials.[8-11] By far, only the *Chevrel* phase compounds show good Mg^{2+} ions intercalation characteristics, but diffusion of Mg^{2+} ions is rather slow and the rate capability is limited at room temperature.[12, 13]

As an alternative to develop cathode materials for intercalating Mg^{2+} ions, here we desire to fabricate batteries by combining Mg and Li electrochemistry. The structure of these batteries is illustrated in Figure 1 and has a Mg metal anode, a Li^+ ion intercalation cathode (Mo_6S_8), and a dual-salt electrolyte with both Mg^{2+} and Li^+ ions (all-phenyl complex (APC) and LiCl dissolved in THF). Such a design is attractive because it could potentially combine the advantages of different types of battery technology. It should be noted that a similar design has been discussed in a previous study,[14] but it appears that prototypes fabricated in that work have some limitations (for example, low coulombic efficiency and short cyclic life), and therefore it is not evident that the design is indeed practical. The hybrid batteries studied in this work had excellent rate capability, superior safety and reliability with reasonable discharge voltages. Prototype batteries were cycled for 3000 times and showed very little capacity fade (~5%). Close examination of the Mg metal after 3000 cycles showed that the surface was clean and smooth, with no obvious formation of dendritic structures. The hybrid batteries discussed in this work could be very promising for practical applications.

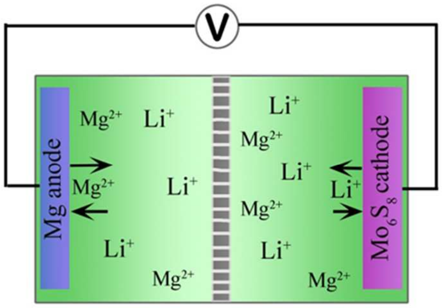

Figure 1: Schematic illustration of the hybrid battery designed in this work. This battery has a piece of Mg foil as the anode, Mo_6S_8 as the cathode, and the electrolyte contains both Mg^{2+} and Li^+.

The Mo_6S_8 materials used in this work was synthesized using the molten salt method by following a reported procedure.[15] The APC electrolyte was synthesized by reacting phenylmagnesium chloride with $AlCl_3$ in THF, followed by addition of an appropriate amount of LiCl (0.4 M APC and 1.0 M LiCl).[16] The battery cells were assembled inside an argon-filled glove box using 2032-type coin cells. All electrochemical tests were conducted at ambient conditions (see supporting information for details).

Mo_6S_8 is known to be capable of intercalation reactions with either Li^+ or Mg^{2+} ions, and the reactions with Li^+ ions have better kinetics.[17] Our results show that Li^+ ions intercalation was the dominant reaction when both Mg^{2+} and Li^+ ions were present, and this is the fundamental basis for the design of Mg/Li hybrid devices. Figure 2a compares the CV profiles of Mo_6S_8 electrodes acquired in APC electrolytes with and without LiCl (other cell parameters were identical). In electrolytes containing LiCl, the anodic and cathodic peaks had better defined shapes with more positive potentials, and the profiles were identical to those of pure Li^+ ion intercalation (three stages with relative stoichiometry 1:2:1).[17, 18] The elemental composition of Mo_6S_8 after a full discharge process in electrolytes containing LiCl was analyzed by energy-dispersive X-ray spectroscopy (EDS) and the results showed no appreciable Mg content (Figure S1). Based on these results, it is evident that Li^+ ions intercalation was the main cathode reaction in hybrid cells and the electrochemical reactions were the following:

$$\text{Anode reaction: } 2Mg \leftrightarrow 2Mg^{2+} + 4e^-$$

$$\text{Cathode reaction: } Mo_6S_8 + 4Li^+ + 4e^- \leftrightarrow Li_4Mo_6S_8$$

$$\text{Overall reaction: } 2Mg + Mo_6S_8 + 4Li^+ \leftrightarrow Li_4Mo_6S_8 + 2Mg^{2+}$$

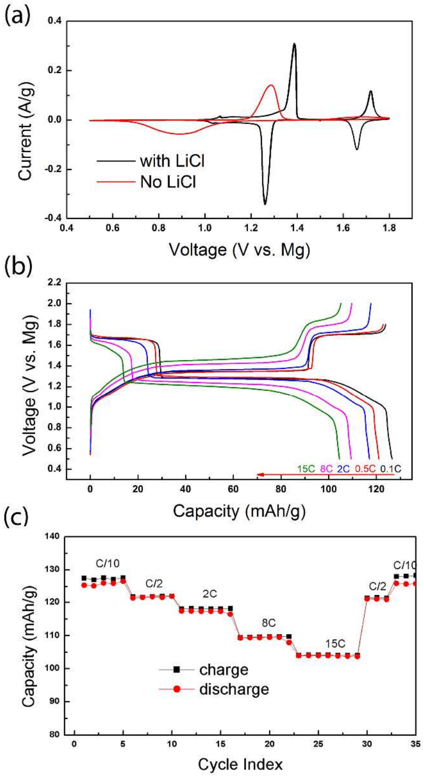

Figure 2: Set of electrochemical testing results: (a) cyclic voltammogram of Mo_6S_8 in APC electrolyte with and without LiCl at a scan rate of 50 μV/s; (b) typical charge-discharge profiles of a hybrid cell at different C-rates and (C) comparison of the specific capacity at different C-rates.

Figure 2b shows typical charge-discharge profiles of a hybrid cell operated at different C-rates (1C is equivalent to 128.8 mA/g). The hybrid cells had two well-defined discharge plateaus at 1.66 V and 1.29 V. The cell had a specific capacity of 126 mAh/g at 0.1C, which is very close to the theoretical capacity of Mo_6S_8 (128.8 mAh/g). It should be noted that the capacity was calculated based on the mass of Mo_6S_8. The theoretical capacity calculated based on the mass of $Mg_2Mo_6S_8$ and $Li_4Mo_6S_8$ are 121.7 and 124.6 mAh/g, respectively. The capacity had slight decreases with increases of C-rate, and was able to maintain 105 mAh/g at a 15C (83% retention, Figure 2c). The realization of capacity close to the theoretical value at low C-rates and the high capacity retention ratios at increased C-rates for hybrid cells were in strong contrast with cells assembled with the APC electrolyte only (i.e., no Li^+ ions; data shown in Figure S2). In the latter case, the reversible capacity was much lower (~80 mAh/g, 0.1C) and faded rapidly with increases of C-rates.

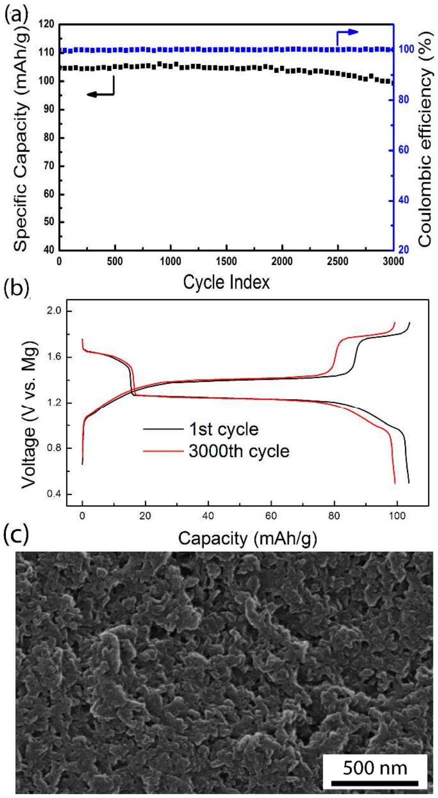

Figure 3: (a) Typical cyclic stability of hybrid cells tested at 10C (1.28 A/g) for 3000 cycles; (b) Comparison of the charge-discharge profiles for the first cycle and the 3000th cycle, showing minimal changes upon repeated charge-discharge operations; (c) Typical SEM image of the Mg anode after 3000 cycles. Note that no obvious dendritic structures were observed.

The electrochemical deposition and stripping processes of Mg^{2+} ions in the APC electrolyte have excellent kinetics and reversibility,[19] making Mg metal ideal for batteries designed for long-term stability. In this work, the cyclic stability of hybrid batteries was studied with a 3000-cycle charge-discharge test conducted at 10C. Figure 3a shows a typical cyclic stability profile and coulombic efficiency as a function of cycle numbers. The hybrid cell was very stable, with close to 100% coulombic efficiency for each cycle and only had ~5% capacity fading after 3000 cycles. The charge-discharge profiles for the first cycle and the 3000th cycle are compared in Figure 3b. The plateau profiles were similar to each other and no significant change was observed other than a ~5% decrease in capacity (maintained at ~100 mAh/g). It has been shown that evaporation of the solvent (THF) was a major cause of capacity fading for rechargeable Mg batteries,[12] and this is likely one of the causes of the capacity fade observed in this work. Figure 3c show a scanning electron microscopy (SEM) image of the Mg anode after it was cycled 3000 times. Unlike the case for Li metal, no obvious dendritic structure was observed on Mg surface (Figure S6 for cross-section SEM). This observation suggests that Mg anode is unlikely to have the safety problems associated with formation of dendritic structures. Such superior cyclic stability is an important feature of Mg/Li hybrid batteries.

The results discussed above demonstrate that the hybrid cells designed here could combine the advantages of Mg and Li electrochemistry and have outstanding rate performance and cyclic stability. Practically, however, the performance of hybrid cells will depend strongly on their assembly methods (in particular, active material loadings relative to amounts of electrolytes) due to their unique operation principle. In particular, the electrolyte should be able to supply sufficient Li^+ ions for the cathode electrochemical reaction and intercalation kinetics, since the Mg/Li battery was assembled at charged state. In this work, we studied the effect on battery performance of the ratio between amount of Li^+ ions in the electrolyte and amount of Li^+ ions required for complete cathode reaction by controlling electrolyte concentration. Our results show that the batteries were able to deliver close to the theoretical capacity at ratios higher than 3, and at lower ratios the cells had much lower capacity and behaved similarly to pure Mg^{2+} ion intercalation (Figure S3, tested at C/5). Therefore, the hybrid batteries will have minimum requirements on the amount of electrolytes for optimal performance. The volume of electrolytes could be reduced by developing novel electrolytes, such as the solvent-in-salt type electrolyte developed recently for a Li-S battery.[20] In principle, it is possible to adopt most Li cathode materials to develop Mg/Li hybrid battery. However, developing electrochemically stable Mg/Li dual salt electrolytes is an immediate technical hurdle, since most known Mg electrolytes have stable electrochemical windows less than 3 V. Research for developing new electrolytes to increase the voltage of hybrid batteries is underway.

In summary, we studied the design of hybrid batteries by combining Mg and Li electrochemistry in one device. This device has a Mg anode, a Li^+ ions intercalation cathode and a dual-salt electrolyte contains both Li^+ and Mg^{2+} ions. Experimental results show that these batteries were able to combine the advantages of different materials and delivered outstanding rate performance (105 mAh/g at 15C) and superior cyclic stability (~5% capacity drop for 3000 cycles at 10C), along with reasonable output voltages. The inherent safety and reliability features of such devices make them very promising for many applications, especially for large-scale static energy storage. The design of batteries discussed and studied in this work could also provide a new approach to high performance energy storage systems.

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Notes and references

Energy Processes & Materials Division, Pacific Northwest National Laboratory, Richland WA, 99354, United States
E-mail: jun.liu@pnnl.gov, guosheng.li@pnnl.gov

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