High-Energy-Density Rechargeable Mg Battery Enabled by a Displacement Reaction

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Supporting Information

ABSTRACT: Because of its high theoretical volumetric capacity and dendrite-free stripping/plating of Mg, rechargeable magnesium batteries (RMBs) hold great promise for high energy density in consumer electronics. However, the lack of high-energy-density cathodes severely constrains their practical applications. Herein, for the first time, we report that a CuS cathode can fully reversibly work through a displacement reaction in CuS/Mg pouch cells at room temperature and provide a high capacity of ~400 mA h/g in a MACC electrolyte, corresponding to the gravimetric and volumetric energy density of 608 W h/kg and 1042 W h/L, respectively. Even after 80 cycles, CuS/Mg pouch cells can maintain a high capacity of 335 mA h/g. Detailed mechanistic studies reveal that CuS undergoes a displacement reaction route rather than a typical conversion mechanism. This work will provide a guide for more discovery of high-performance cathode candidates for RMBs.

KEYWORDS: Rechargeable Mg batteries, cathode materials, high energy density, displacement reaction, CuS
1.9 V vs Mg/Mg$^{2+}$ and does not accomplish complete reversibility of the CuS cathode, thus only $\sim$14% of the theoretical capacity is achieved.

Herein, we, for the first time, demonstrate that CuS secondary microspheres assembled with primary CuS nanoparticles can fully reversibly work in pouch cells at RT through the
displacement reaction. The CuS/Mg pouch cell can achieve a high reversible capacity of ~400 mA h/g (≈71% of the theoretical capacity) between 0.5 and 2.2 V for the first three cycles, corresponding to a volumetric energy density of ~1042 W h/L (more than twice that of the LiCoO2/graphite pouch cell: 491 W h/L)1–3 and a gravimetric energy density of 608 W h/kg. After 80 cycles, the CuS/Mg pouch cell is able to provide a capacity of ~335 mA h/g at 1.52 V, corresponding to the volumetric energy density of ~872 W h/L, much higher than that of Li−O2 and Zn−O2 batteries. Through mechanistic and kinetics investigations, we demonstrate that CuS undergoes a displacement reaction, and the fast diffusion of Cu favors the fast magnesiation and demagnesiation of CuS.

CuS was prepared by a modified hydrothermal method.50 The phase of CuS microspheres is confirmed with powder X-ray diffraction (XRD). The characterized peaks match well with the standard card of JCPDS no. 06-0464 (Figure 1a), with the P63/mmc space group, consistent with previous reports. SEM images show that the CuS secondary microspheres have a diameter of 2 to 3 μm (Figure 1b), which are assembled by primary nanoparticles (~200 nm) (Figure 1c). This configuration is important because the kinetics of magnesiation is limited by solid-phase diffusion.9,22 The short ionic diffusion length provided by the primary nanoparticles should alleviate the resistance against magnesium ion diffusion in the solid phase and improve the electrode kinetics. The secondary particles have a size comparable to that of commercial LiFePO4 particles,31,52 which enables the high stacking density essential to achieving a reasonable volumetric energy density in practical application and reduces the side reaction of CuS with electrolytes.

The electrochemical performance of CuS/Mg pouch cells was examined with MACC as the electrolyte and Mg foil as the negative electrode at RT (Figure 2). A molybdenum grid is used as the current collector, which is stable in MACC electrolyte until 2.8 V (Figure S1). The discharge/charge curves of the first three cycles are shown in Figure 2a. The first discharge (Mg2+ insertion) capacity reaches ~430 mA h/g, with two plateaus at 1.4 and 1.15 V, corresponding to 76.8% of the theoretical capacity of CuS with two electrons transferred (~560 mA h/g). The first plateau at ~1.4 V delivers a capacity of ~203 mA h/g, corresponding to 0.36 Mg2+ transfer, and the second plateau at ~1.15 V achieves a capacity of 227 mA h/g, corresponding to 0.41 Mg2+ transfer. When recharged to 2.2 V, two plateau of ~1.64 and 2.1 V can be clearly observed, with 96% of inserted Mg2+ extracted (413 mA h/g). In the following cycling, both discharge and charge curves almost overlap, indicating a reversible reaction process (Figure 2a). The overpotential between discharge and charge processes is ~0.4 V (after excluding the overpotential of ~0.1 V in the Mg negative electrode (Figure S2)), which is much lower than for many cathode materials for RMBs53–55 and even lower than many conversion cathodes for LIBs.46,57 SEM and EDS were employed to confirm that there is no transport of Mg sulfide to the Mg anode (Figure S3). Within the first three cycles, a reversible capacity of ~400 mA h/g is maintained, corresponding to a gravimetric energy density of 608 Wh/kg, which until now is the highest among all of the reported intercalation and conversion cathodes for RMBs.46,57,58

Long-term cycling performance of the CuS/Mg system was evaluated with a MACC electrolyte at 5 mA/g and RT (Figure 2b). The rapid loss of capacity for the first 10 cycles can be attributed to some Mg2+ trapped in CuS, indicated by a low Coulombic efficiency (less than 99.4%). In addition, the dissolution of copper ions into electrolyte also leads to a

Figure 3. (a) Quasi-equilibrium voltage profile of the CuS/Mg system obtained from GITT. The cells were allowed to relax for 8 h after every 2 h of discharging or charging at 5 mA/g and RT. (b) Comparison of an experimental (black) and theoretical (blue) equilibrium voltage curve for CuS, after excluding the overpotential in the Mg negative electrode. (c) Close-up view of the GITT curve. The IR drop, reaction overpotential (η), and the remaining voltage difference after relaxation (Vgap) are marked to show the components that contribute to the voltage gap during cycling. (d) Absolute value of the voltage difference (IR+η) for the system with current on and after 8 h of relaxation for the discharging and charging process. (e) Representation of the transient voltage of the galvanostatic pulse as a function of the square root of the time for CuS. The red dashed line is the linear fitting, and the slope of the linear fitting is presented in the plot.
capacity loss (Cu concentration in cycled MACC electrolyte: 1.29 ppm according to ICP), which is common in copper-based cathodes. The CuS/Mg full cells hold a capacity of ~335 mA h/g after 80 cycles, which is much higher than that previously reported for CuS because of the unique aggregated structure of CuS. To highlight the advantage of CuS microspheres, the electrochemical performance of commercial CuS (with an average diameter of ~10 μm) (Figure S5) was also evaluated under the same testing conditions. The capacity of 26 mA h/g is delivered in the first discharge, whereas a negligible charging capacity (12 mA h/g) is achieved (Figure S6a). Very short voltage plateaus are presented with large polarization. No improvement in capacity occurs after 10 cycles (Figure S6b), which is in agreement with the results reported by Duffort et al. at RT and 60 °C. It further validates the advantages of the microsized secondary particles with respect to kinetics.

To further demonstrate the merits of CuS secondary microspheres, higher current densities were applied (Figure 2c). Even at 50 (C/10) and 100 mA/g (C/5), CuS/Mg full cells still achieve high capacities of 260 and 190 mA h/g, respectively, which are much better than those reported for CuS cathodes, corroborating the fast magnesiation kinetics of CuS. We also conservatively evaluated the volumetric energy density of the Mg pouch cell, according to Aurbach et al., if the capacity (400 mA h/g) of CuS at 1.52 V is taken into account (Table S2). By applying the same method, the diffusion coefficient for Mg in CuS at different charge/discharge states can also be obtained from GITT using eq 1.

\[
D = \frac{4}{\pi} \frac{IV_M}{Z_A FS} \left[ \frac{dE}{dx} \right]^2 \left[ \frac{dE}{dt} \right]^2
\]

where \(D\) is the applied constant current, \(V_M\) is the molar volume of CuS (20.09 cm³/mol), assumed to be constant during the electrochemical process, \(Z_A\) is the charge number of electroactive species Mg²⁺, \(F\) is the Faraday constant (96 486 C/mol), \(S\) is the electrochemical active area between the electrode material and electrolyte from the Brunauer–Emmett–Teller (BET) surface area \((S_{BET} = 17 870 \text{ cm}^2/\text{g})\) (Figure S7a), \(E(x)\) is the steady-state equilibrium voltage (i.e., open circuit voltage) of the working electrode (vs the reference electrode) at the composition of Mg, CuS, and \(E(t)\) is the transient voltage response of the working electrode during the constant current interval.

Equation 1 could be applied only in solid-solution materials, not in the phase-transition regions, in which the value of \(dE/dx\) should be zero according to the Gibbs phase rule. We calculated only the ion diffusion coefficient in the solid-solution region near the end of discharging and charging. The transient voltage versus the square root of the time was plotted in Figure 3e. Plugging the slope of the linear fitting into eq 1, we can get the diffusion coefficient of Mg²⁺ in CuS for the first discharge plateau to be 1.97 × 10⁻¹⁴ cm²/s, which is higher than that of LiFePO₄ (6.77 × 10⁻¹⁶ cm²/s). Actually, the higher diffusion coefficient does not dictate a faster reaction because the magnesiation of CuS is a phase-transition reaction whose rate not only depends on the diffusion rate but also relies on the speed of the phase transition.
which $t$ represents the diffusion time and $L$ represents the diffusion length), reducing the particle size will shorten the ionic diffusion path as well as the diffusion time, which is an effective method of improving the kinetics. It also explains why commercial CuS ($\sim 10 \mu m$ according to Figure S4) delivers only a negligible capacity in this paper and that by Duffort et al.,\textsuperscript{46} whereas CuS secondary microspheres assembled by nanoparticles ($\sim 200 \text{ nm}$) achieve a high capacity.

The reaction mechanism of CuS with Mg was investigated by ex situ XRD, XPS, SEM, TEM, and EDS during the first cycle (Figures 4 and S8–S13). For ex situ XRD, during Mg insertion (discharge) (from A to B), Cu$_2$S (PDF no. 26-1116) and MgS (PDF no. 65-0895) peaks emerge before 1.2 V, with the intensity of CuS drastically decreasing, indicating that reaction II occurs. However, because of sluggish kinetics, reaction II is not accomplished completely, leaving some CuS unreacted, which is consistent with the fact that the corresponding capacity (203 mA h/g) is less than the theoretical capacity of reaction II (280 mA h/g). Upon further discharge (from B to C), peaks for MgS are enhanced, with Cu peaks (PDF no. 65-9026) emerging and Cu$_2$S peaks weakened, suggesting that reaction III proceeds. Also, reaction III is not completed, in accordance with the corresponding capacity of 227 mA h/g (81.1% of the theoretical capacity). Upon recharge (from C to D), MgS and Cu peaks gradually recede, indicating that reaction III proceeds in the inverse direction, with the charge capacity of 160 mA h/g being less than the discharge capacity on the second voltage plateau (227 mA h/g). When the CuS/Mg system is fully recharged to 2.2 V (from D to E), the final charged product is back to CuS. In the following discharge/charge cycles, reactions II and III proceed reversibly. The reaction equations are the following:

\[ \text{CuS} + 0.5\text{Mg}^{2+} + e^- \leftrightarrow 0.5\text{Cu}_2\text{S} + 0.5\text{MgS} \quad \text{(II)} \]

\[ 0.5\text{Cu}_2\text{S} + 0.5\text{Mg}^{2+} + e^- \leftrightarrow \text{Cu} + 0.5\text{MgS} \quad \text{(III)} \]

The reaction mechanism is further confirmed by ex situ XPS (Figure 4c), in which the C 1s peak at 284.8 eV is used as a reference binding energy (Figure S8). During discharging from A to B, the binding energy increases from 932.55 to 932.62 eV, indicating that CuS is transformed to Cu$_2$S.\textsuperscript{71,72} Upon further discharge to C (the fully discharged state), the binding energy of 932.71 eV represents the appearance of metallic copper,\textsuperscript{73} which is the final product of the discharging process. In the following recharging process, the binding energies of 932.63 eV (at point D) and 932.54 eV (at point E) indicate the reformation of Cu$_2$S and CuS, respectively. Therefore, the Mg insertion/extraction of CuS is highly reversible, which is consistent with the results of ex situ XRD. However, the oxidation state of sulfur does not change with the cycle (Figure S9), indicating that Cu is the only redox-active element in the magnesiation/demagnesiation of CuS.

Energy-dispersive X-ray spectroscopy (EDS) was also conducted to investigate the magnesiation mechanism of CuS (Figure S10). Five electrodes on different discharge/charge states (from A to E) indicate that the amount of inserted Mg corresponds well to the specific capacity.

To thoroughly investigate the magnesiation mechanism of CuS, we re-examined the discharge/charge characterizations. Because the first discharge potential of a conversion reaction is always lower than that in the following discharging process, which is a typical characteristic of the conversion cathode, the absence of a voltage difference between the first and second discharging processes suggests that a displacement rather than a conversion reaction seems more likely (Figure 2a).\textsuperscript{74} SEM, TEM, and EDS are applied to reveal the displacement reaction (Figures 4d–f and S11–S13). Fully discharged to 0.5 V, a large amount of Cu dendrite can be found in different-magnification SEM images, which is highlighted by red arrows (Figure S11), in
contrast to no Cu dendrite in other discharge/charge states (Figure S12). TEM images of an electrode discharged to 0.5 V clearly reveal that large Cu dendrites (several micrometers long) grow out toward the core particles (Figure 4d,e). EDS demonstrates that the dendrite is metallic copper (Figure 4d), which is further confirmed by HRTEM and FFT (Figure 4e).

The crystal structure of CuS and discharged product MgS is examined (Figure S14). The projected structure of CuS and MgS is drawn along the [001] and [110] directions, respectively, in which the sulfur atoms form in a layer stacking sequence. Between these sulfur layers, the copper and magnesium cations make zigzag chains and a straight line, respectively. When Mg ions are “inserted” into the CuS material, they “insert” between the sulfur layers and drive out copper cations with high mobility to form a metal copper dendrite, which undergoes a displacement reaction. It has been reported that Li insertion/extraction into CuS also occurs through displacement, providing 550 mA h/g (98% of its theoretical capacity). Upon lithiation, the insertion of the guest cations (Li+) will induce the displacement and extrusion of transition-metal cations (Cu2+) from original sites, with Cu2+ reduced to Cu0, which might be isolated as a metal precipitate. Upon charging, Cu0 is reoxidized to Cu2+ and injected into the host structure, replacing the Li+ in the discharged products. The high Cu mobility via a vacancy mechanism is the key to achieving the displacement, which will contribute to the improved kinetics of cathode materials. The fast displacement kinetics of CuS with Mg enables fast Mg2+ in CuS and a low overpotential of less than 0.4 V. The fast reaction kinetics of CuS with Mg2+ results in strong interaction between Mg2+ with CuS and slower reaction kinetics of CuS in RMBs.

We, for the first time, demonstrated the fully reversible CuS cathode through a displacement reaction in CuS/Mg pouch cells at RT, which delivers a reversible capacity of ~400 mA h/g for the first three cycles between 0.5 and 2.2 V, corresponding to a volumetric density of 1042 W h/L, which is much higher than for LiCoO2-graphite (491 W h/L). A capacity of 335 mA h/g is maintained after 80 cycles. At higher current densities of 50 (C/5), and 100 mA/g (C/10), CuS/Mg full cells still achieve capacities of 260 and 190 mA h/g, respectively, indicating the fast magnesiation kinetics. Two-step reactions with two equilibrium potential plateaus obtained from GITT are validated by the projected structure of CuS and almost identical discharge curves in XRD, XPS, SEM, TEM, and electrochemical performance (PDF).

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**Notes**

The authors declare no competing financial interest.

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