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Electrochemically Stable Cathode Current Collectors for Rechargeable Magnesium Batteries

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Rechargeable magnesium (Mg) batteries are attractive energy storage systems that could yield cost-effective energy solutions. Currently, however, no practical cathode current collector that can withstand more than 2.0V in Mg²⁺ electrolytes has been identified; this greatly hinders cathode research. Here we identified that Molybdenum (Mo) and Tungsten (W), are electrochemically stable (>2.8V) through formation of passive surface layers. The presented results could have significant impact on the development of high voltage Mg batteries.

The increasing energy crisis and interest in sustainable energy management have induced substantial investments in advanced energy storage systems.¹ Lithium-based batteries are currently widely used but the predicted high demand associated with many large-scale applications has generated serious concerns regarding their safety and sustainability.² Recently, considerable effort has been devoted to developing alternative energy storage technologies.^{3, 4} In particular, Mg-based batteries have attracted increasing attentions because they could lead to low-cost and high energy density devices with improved safety.⁵ Key benefits of Mg batteries include potentially much lower cost since Mg metal costs 24 times less than Li metal, and superior safety since Mg metal is air stable and Mg ions can be deposited onto Mg metal without formation of dendritic structures.⁶ The latter feature could enable design of systems with remarkably high energy density with Mg metal as their anodes, since Mg metal has a theoretical volumetric capacity of 3,832 Ah/L, which is much higher than 2,062 Ah/L for Li metal.

The fundamental components of rechargeable Mg batteries are similar to other batteries and include Mg metal anode, cathode, current collector, electrolyte, separator and cell case. Among these, electrolyte and cathode are two unique components for Mg batteries and require special design and engineering.^{7, 8} Over the past few years significant progress has been achieved on the development of Mg electrolytes. In addition to nonaqueous electrolytes, ionic liquid, gel, polymer and solid-state polymer based electrolytes have also been proposed and developed.⁹⁻¹¹ When considering Mg deposition/stripping efficiency and anodic stability, the most promising electrolytes are based on magnesium organohaloaluminate species dissolved in tetrahydrofuran

(THF).¹²⁻¹⁴ A notable example is the all-phenyl-complex (APC) based electrolyte that has electrochemical windows ~ 3.3 V vs. Mg as recently developed by Aurbach *et al.*¹⁵ Even though these electrolytes perform excellently for Mg anode, they all contain high concentrations of chloride anion and are corrosive to almost all of the metals and alloys that have been conventionally used as current collectors and cell cases for batteries.^{13, 16} The anodic behavior of typical metals (such as Fe, Cu and Al) in these electrolytes have been studied but almost all of them have stability lower than 2.0 V vs Mg,¹⁷⁻¹⁹ and no practical metal with stability comparable with Pt has been identified yet. This fact has significantly constrained the development of Mg batteries. As of now the best cathode (in terms of capacity and cyclic stability) developed is based on Mo₆S₈ with voltages of ~1 V, and very few cathode materials with voltages exceed 2 V have been demonstrated.^{8, 20} Given the critical importance of voltage to the practical merits of a battery system, it is therefore evident that developing high voltage cathode materials is one of the keys to successful widespread application of Mg batteries.⁸ As a first step, it is necessary to identify practical materials (metals, alloys or other materials) that are electrochemically stable in Mg²⁺ electrolytes and have stability windows comparable to Pt and glassy carbon to be used as the materials for current collectors and cell cases.

The purpose of this study was to identify appropriate metals that have appreciable anodic stability in electrolytes developed for rechargeable Mg batteries. Two types of electrolytes were used, namely an APC electrolyte and a novel electrolyte recently developed by Liu *et al.*²¹ because they both possess excellent electrochemical stability and high Mg deposition/stripping efficiency. The metals examined were Mo, W, stainless steel (SS) and Cu. For control purposes, both Pt and glassy carbon electrodes were also studied. Several other metals, such as Ni, Ti and Al, have been studied previously¹⁷⁻¹⁹ and are known to have limited anodic stability (< 2.2 V) and therefore were not included in this study.

The electrochemical behavior of these four subject metals, along with Pt and glassy carbon, was first examined using cyclic voltammetry (CV) in a potential range of -0.5~3.5 V vs. Mg with 10 mV/s and a three-electrode setup. All the experiments were performed inside a nitrogen-purged glove box at room temperature. The metals were used as the working electrodes and two pieces of Mg ribbon were used as the

reference and counter electrodes. Each piece of metal foil was polished thoroughly and washed repeatedly with THF inside a glove box to remove surface contaminants. Their exposure areas in electrolytes were controlled to be similar (3×2 mm). Typical results are shown in Figure 1. On all of the working electrodes, the peaks corresponding to Mg deposition and dissolution were observed around 0 V (Mg deposition for the peaks below 0 V and Mg dissolution for the peaks in the range of 0 ~ 1.0 V). As expected, Pt and glassy carbon electrodes were both stable over the entire potential range, and appreciable anodic currents were only observed beyond 2.8 V due to oxidative decomposition of the electrolyte.²² Among the metal foils, very interesting behaviors from Mo and W were observed. They were both stable and behaved similarly to Pt and glassy carbon in term of anodic stability, and no appreciable anodic current corresponding to electrode dissolution or cathodic current corresponding to deposition of dissolved ions (if any) in the potential range of 0~2.8 V were observed. The increases in anodic current beyond 2.8 V were due to decomposition of the electrolyte, which was also observed on Pt and glassy carbon electrodes.

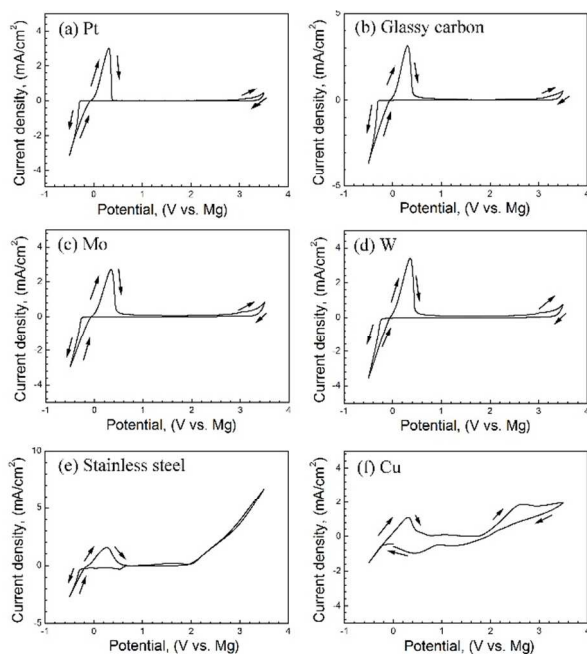


Figure 1: Cyclic voltammograms (second cycle) recorded using different working electrodes in 0.25M APC electrolyte. The scan rates were all 10 mV/s.

To further confirm the stability of Mo and W, scanning electron microscopy (SEM) was used to examine the changes in their surface morphologies before and after CV cycles, and their typical images are compared in Figure 2a (for Mo) and 2b (for W). Note that a 1000-cycle test was used here in order to examine their long-term stability. As can be seen, no obvious changes in surface morphology were observed even after 1000 cycles. If these metals were not stable under anodic polarization, features corresponding to corrosion of current collectors (such as pitting) should be easily spotted (as is the case for SS and Cu, shown in Figure 2c and d).²³ Furthermore, the APC electrolytes remained clear and the Mg counter

electrodes remained shiny after testing with Mo and W, whereas they both turned black when tested with SS and Cu. These visual observations indicate no obvious side-reactions happened with Mo and W. Therefore, it is evident that both Mo and W were electrochemically stable over the potential range studied and the surface morphologies were unchanged after cycling in the APC electrolyte.

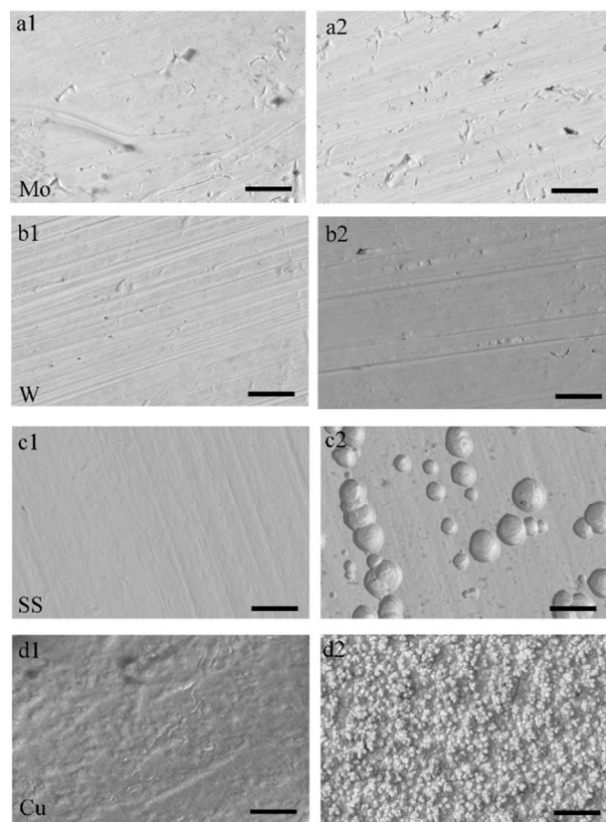


Figure 2: SEM images of (a) W, (b) Mo, (c) Cu and (d) SS electrodes before (left) and after (right) CV scan between -0.5 and 3.5 V vs. Mg in APC electrolytes. The scale bars are all 20 μ m.

The behavior of SS and Cu as the working electrodes were also studied using identical methods (results are shown in Figures 1 and 2). In strong contrast to Mo and W, both SS and Cu had very inferior stability. As can be seen in Figure 1e, an oxidative peak beginning at 1.2 V in the CV curve was observed when a SS foil was used as the working electrode. This peak can be attributed to the oxidative corrosion of SS since the electrolyte was stable in this range, and therefore the stable anodic range of SS was only 1.2 V. The SEM images shown in Figure 2c also show clear changes in the morphology of the foil. Similarly to SS, an obvious anodic peak was observed at ~1.7 V for the Cu electrode. Comparison of the SEM images shown in Figure 2d clearly shows that the initially smooth surface was damaged during the CV scan. These results agree well with previous studies.^{17, 18}

In a chloride-rich environment (as chloride is present in both the cation and anion components of the APC electrolyte), the predominant corrosion mechanism for metals is through reactions with chloride anions.¹³ In fact, our analysis on the

order of stability limits (E) of different metals ($\text{Cu} > \text{Ni} > \text{Fe} > \text{Ni} > \text{Al}$) using our data as well as reported data¹⁸ revealed that it corresponds well with the order of the free energy of formation (ΔG) of their chlorides on the basis of $\Delta G \propto -n\Delta E$. The apparent stability of Mo and W observed in this work, however, cannot be explained through thermodynamic considerations, as the ΔG s of their chlorides (MoCl_2 : -144.9 kJ/mol; WCl_6 : -548.9 kJ/mol) are comparable with that of CuCl_2 (-175.7 kJ/mol) after accounting for the number of transferred electrons. Therefore, a protection mechanism seems exist to account for their appreciable electrochemical stability in the APC electrolyte.

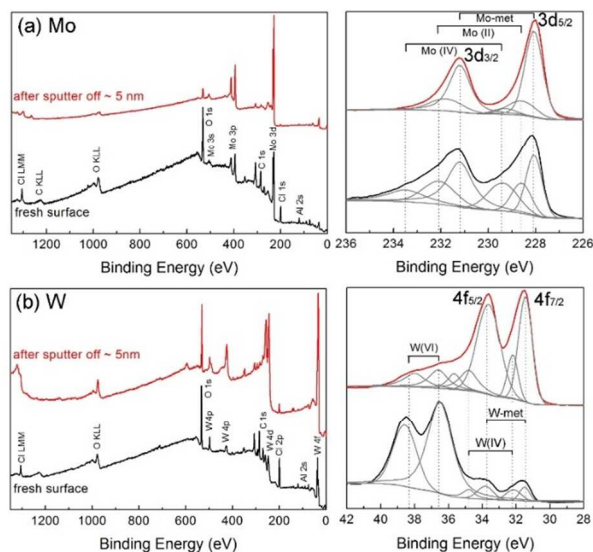


Figure 3: XPS spectra of (a) Mo and (b) W foils after 1000 CV cycles in APC electrolyte, both for the fresh surface and for the underlying surface after sputter removal ~ 5 nm as noted.

In general, the corrosion resistivity of a material depends on the reaction products formed on its surface, as well as the stability of the products.²⁴ On the basis of X-ray photoelectron spectroscopy (XPS) measurements for both the fresh surface and the underlying surface after 5 nm was sputtered off using Ar ions, the presence of passive layers on Mo and W was clearly identified. In this paper, the term “fresh surface” refers to the as-prepared surface after 1000 CV cycles. As shown in Figure 3, both the fresh and underlying surfaces showed substantial levels of oxygen and chlorine after being cycled in the APC electrolyte. Since the foils were polished extensively and washed repeatedly with THF in a glove box prior to all tests, such recognizable chlorine and oxygen contents were most likely introduced by the electrochemical tests. Even though levels of both were decreased remarkably after sputtering, their presence was still noticeable. The spectrum for the fresh Mo surface in the Mo 3d region showed several components. The spectral lines at 228.0 and 231.2 eV were from the metallic Mo $3d_{5/2}$ and $3d_{3/2}$ spin-orbit components, respectively.²⁵ The spectral lines at 228.6 and 231.8 eV could be assigned to Mo(II) and they match best with those of MoCl_2 .²⁶ The spectral lines at 229.3 and 233.4 eV were most

likely from Mo(IV) and they are close to the reported values for MoO_2 and MoCl_4 .^{25, 27} Since the XPS signals of high Mo-valence chlorides and oxides have significant overlap, it is likely both of them exist in the film. After sputtering, the intensities of spectral lines corresponding to Mo(IV) decreased remarkably and the spectrum was mainly from Mo(II) and metallic Mo. These results indicate that the composition of the passivation film was likely not uniform, with more Mo(IV) species at the outer surface.

The W 4f spectrum also showed complex chemistry and had several components as shown in Figure 3b.²⁸ The spectral lines at 31.4 and 33.6 eV were from metallic W. On the basis of reported data, the other four spectral lines could be assigned to W(IV) species (32.2 and 34.8 eV) and W(VI) species (36.6 and 38.0 eV).^{28, 29} The W(IV) peaks were at energies lower than typical WO_2 , and this might indicate WO_2 with a non-ionic bond as has been observed previously.²⁸ The W(VI) species is believed to be WCl_6 and/or WOCl_4 as the observed energies were higher than that of WO_3 . Notably, the extent of W(VI) is significantly higher than W(IV) and the passive film was primarily formed with hexavalent tungsten. The composition of the film seems more uniform than that formed on Mo, as the XPS spectrum for the sputtered film showed spectral lines similar to those for the fresh surface. Even though XPS showed complex chemistry of the passivation films, it is clear that Mo and W are both electrochemically stable in the APC electrolyte due to the formation of passive layers. The fact that they were durable for 1000 cycles indicates that the passivation films were very stable. It is likely that the protection layers were a few nanometers thick on the basis of substantially increased metal contents after sputtering. The formation mechanism of oxides is not well understood at present but will be pursuit in follow-up studies.

The excellent electrochemical stability of Mo and W through formation of surface passivation layers has been recognized previously for several applications. For example, they have been suggested for use as cathode current collectors in Li cells.²³ They have also been used to improve the corrosion resistivity of metals and alloys (such as Fe and Al) in chloride-rich aqueous and gaseous environments for industrial applications.³⁰⁻³² On the basis of the present work, we identified that the passive films can also readily form in chloride-rich non-aqueous media and these films were very stable, which makes them promising materials for use as cathode current collectors in rechargeable Mg batteries, where most conventional current collectors failed.

In addition to the APC electrolyte, we also studied the stability of Mo and W in an electrolyte based on MgCl_2 - AlEtCl_2 complex dissolved in THF. This electrolyte has improved conductivity, excellent Mg reversibility, improved nucleophilic and oxidization stability as discussed in detail in our previous paper.²¹ The behaviors of Mo and W in this electrolyte are shown in Figure 4, along with that of Pt for comparison. As can be seen, both of them also have superior stability similar to the Pt electrode. The small anodic peaks at ~ 3.0 V were originated from the electrolyte due to its

irreversible oxidization. These data demonstrate that the superior stability of Mo and W should also apply for other electrolyte systems.

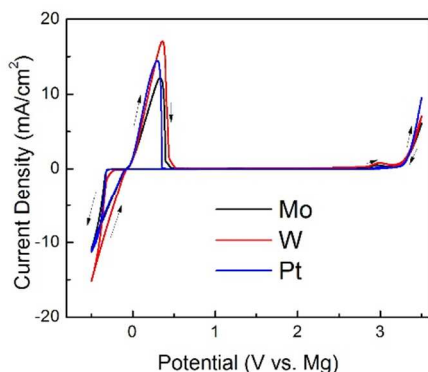


Figure 4: Cyclic voltammograms (second cycle) for Mo, W and Pt working electrodes in a new electrolyte consisting of $\text{MgCl}_2\text{-AIEtCl}_2/\text{THF}$. These data were acquired using a three-electrode setup and scan rate of 10 mV/s.

Conclusions

The current collector is a critical component in all battery systems, and this is certainly also the case for Mg-based batteries. They must be electrochemically stable for the entire operating window of an electrode. The strong corrosive nature of electrolytes developed thus far for Mg batteries posts rigid requirements for their current collectors as well as other cell components such as the cell case. Previous works have identified several potential anode current collectors but no practical cathode current collector has been established. The superior electrochemical stability of W and Mo as demonstrated in this work could have significant impact on the research and development of high voltage and low-cost rechargeable Mg batteries.

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Notes and references

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