Microscopic Characterization of Electrodeposited Mg Layers for Battery Application

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Magnesium has been considered as a strong candidate for metal air battery applications due its low cost, environmentally benignity, high theoretical specific charge capacity (2.205 Ah/g), and high theoretical energy density (3.8 Ah/cm^3) [1, 2]. However, one of the current technical limitations is the understanding of the interactions taking place at the electrolyte/Mg interface. In this study, atom probe tomography (APT) and transmission electron microscopy (TEM) have been successfully applied to the characterization of electrodeposited Mg layers to understand the functionality of electrolytes in Mg deposition.

Mg layers were deposited in a series of electrolytes using a standard 3 electrode cell with working electrode as Au coated-Si wafer, counter electrode as Mg^0, and reference electrode as Mg^0. The compositions of the electrodeposited Mg layers were investigated using atom probe tomography to understand the role of electrolyte functionality in the deposition of Mg. The three electrolytes used were (PhMgCl)$_4$-Al(OPh) (APCC) [3], 2MgCl$_2$:AlCl$_3$ (MACC) [4], both in tetrahydrofuran, and Mg (CF$_3$SO$_2$NSO$_2$CF$_3$)$_2$ (TFSI) in diglyme to explore the effect of electrolyte chemistry. The morphology, structure and chemistry of the deposited Mg layers will be discussed. The deposited films are almost pure Mg (>98 at%) with impurities that include O, C, Al, Cl, MgH$_X$, MgO$_X$. The amount of impurity is slightly lower for MACC electrolyte, while the other two electrolytes yield significant of hydroxide and impurity incorporation. Compositions of Mg layers obtained from the three electrolytes are shown in Table 1.

Efficient Mg deposition/dissolution using a Grignard-based electrolyte is commonly ascribed to the absence of a surface film, which would impact anode performance. The nucleation and growth mechanisms of Mg grains during deposition are important mechanisms to understand to ensure long-term stability of rechargeable Mg batteries. To investigate the interactions with possible surface films, analyses were carried out on Mg layers, for which deposition had been interrupted for some controlled amount of time [5] to let the surface equilibrate with the electrolyte. A TEM cross-section image (Fig. 1a) illustrates the two layers of Mg formed during the interrupted deposition using MACC. APT analysis indicates the presence of C, Al, Al, and Mg oxides/hydrides at the interface (Fig. 1b). Our understanding of the role of the surface film in governing the re-nucleation of Mg onto itself will be discussed in this presentation.

References:
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Table 1: Measured compositions (in at.%) of electrodeposited Mg films deposited using APCC-$(PhMgCl)_4$-$Al(OPh)_3$, MACC-$2MgCl_2$:$AlCl_3$, and TFSI-$Mg(CF_3SO_2NSO_2CF_3)_2$

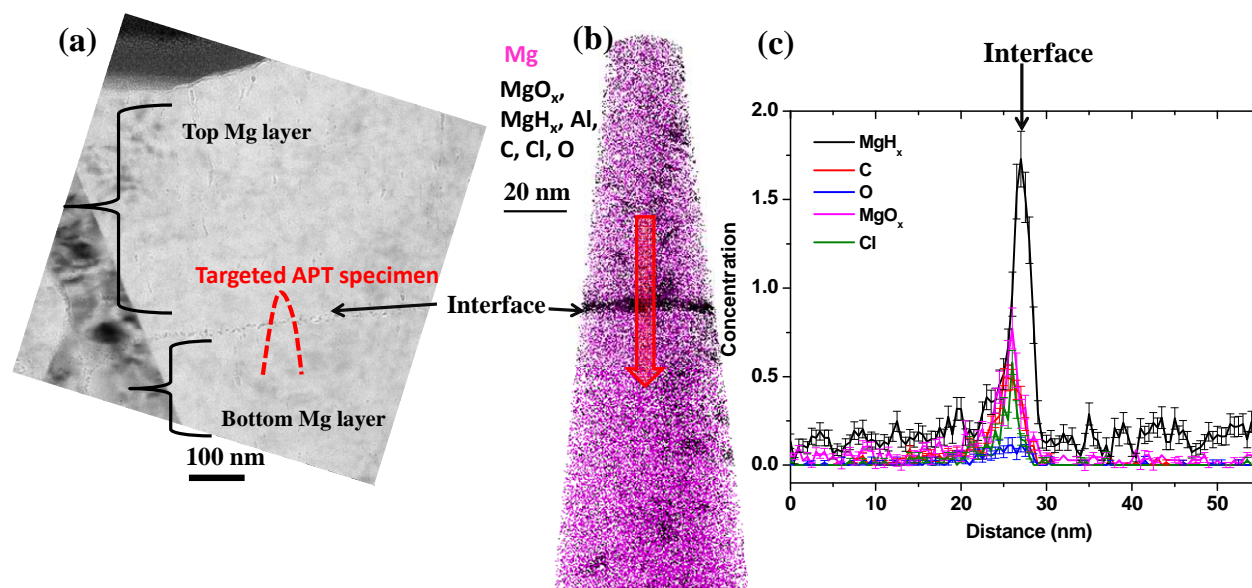| Elements/ions	TFSI	MACC	APCC
Mg	98.2±0.3	99.6±0.2	98.3±0.3
C, O, Cl, MgH_x, MgO_X	1.8±0.3	0.4±0.2	1.6±0.2

Figure 1: TEM image showing two distinct Mg layers marked with site targeted by APT. (b) 3-D reconstruction showing interface and distribution of Mg and impurities. (c) 1D distribution profile taken along interface from top layer to bottom layer