## **Electronic Supplementary Information**

## Mg rechargeable batteries: an on-going challenge

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In general, Al species constitute the anions in the organo-haloaluninate electrolytes. But very small (~1/1000 compared to Mg deposition) cathodic peak was observed before the beginning of Mg deposition (in the insets of Figs. S1 and S2 for DCC and APC electrolytes, respectively). And the potential range (0.2–0.7 V vs. Mg/Mg<sup>2+</sup>) is similar to the redox potential of  $Al^{3+}/Al$  (0.72 V vs. Mg/Mg<sup>2+</sup>). The reason why Al deposition is not dominant in these solutions would be the high Lewis bascity of the surrounding electrolyte, for Al deposition is favored in the Lewis acidic media.<sup>S1</sup> Simpler systems (AlCl<sub>3</sub> in THF with or without the addition of MgCl<sub>2</sub>) shows clearer features of reversible Al deposition/dissolution (Figs. S3 and S4).

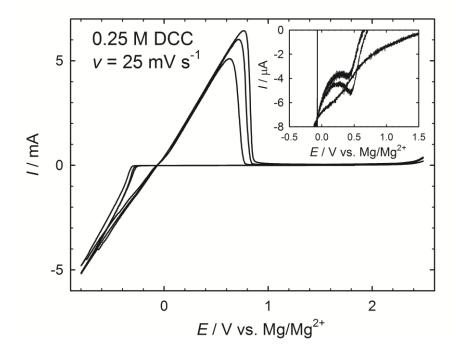


Figure S1 The cyclic voltammogram of 0.25 M DCC electrolyte on Pt substrate (scan rate =  $25 \text{ mV s}^{-1}$ ). The magnified view is in the inset.

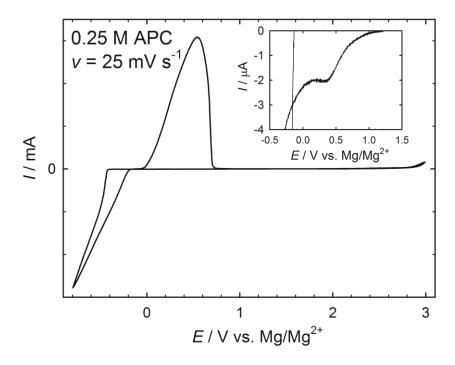


Figure S2 The cyclic voltammogram of 0.25 M APC electrolyte on Pt substrate (scan rate =  $25 \text{ mV s}^{-1}$ ). The magnified view is in the inset.

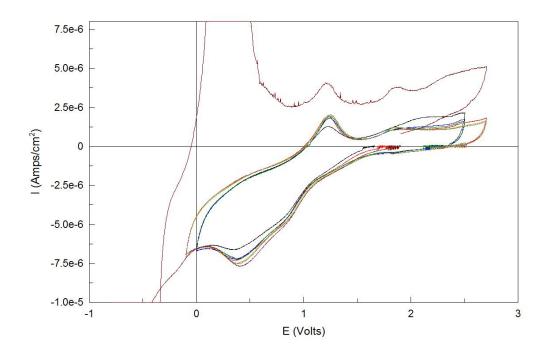


Figure S3 The cyclic voltammogram of 0.157 M AlCl<sub>3</sub> + 0.33 M MgCl<sub>2</sub> in THF on Pt substrate (scan rate = 25 mV s<sup>-1</sup>). The potential was measured with respect to 0 V vs.  $Mg/Mg^{2+}$ . Al deposition and dissolution is clearly observed at 0.5 V and 1.2 V, respectively.

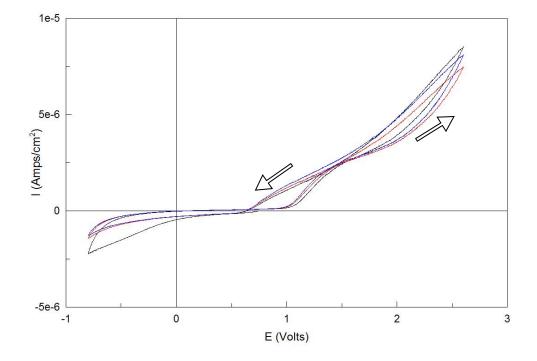


Figure S4 The cyclic voltammogram of  $0.25 \text{ M AlCl}_3$  in THF on Al substrate (scan rate = 25 mV s<sup>-1</sup>). The potential was measured with respect to Mg reference electrode. Al deposition and dissolution is observed at 0.6 V and 1.0 V, respectively.

## Reference

S1 D. Aurbach, in *Nonaqueous Electrochemistry*, ed. D. Aurbach, Marcel Dekker, New York, 1999, ch. 6, pp. 289-409.