Simple Approach to Non-nucleophilic Electrolytes with Good Performance for Rechargeable Magnesium Batteries

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Rechargeable magnesium batteries have been recognized as one of the most promising electrochemical energy storage systems owing to their high theoretical capacity (2205 mA h g^{-1}, 3832 mA h cm^{-3}), low cost of raw material and good operational safety.[1] In contrast to lithium batteries, the solution containing the conventional ionic salts such as magnesium perchlorate [$(Mg(ClO_4)_2$] or magnesium bis(trifluoromethane sulfonyl)-imide (MgTFSI) does not conduct magnesium ions and deposit magnesium metal due to the formation of an electrochemically blocking layer on the anode.[2] Breakthroughs have been achieved by combining an organomagnesium Lewis base such as dibutyl magnesium (Bu_2Mg) or Grignard reagents (RMgCl) with a Lewis acid based on aluminium or boron compounds in THF.[3] Electrolytes enabling the reversible Mg deposition-dissolution with an anodic stability up to 3.5 V *vs.* Mg have been presented.[3] However, due to their common nucleophilic properties, they are incompatible with some potential high energy conversion cathode materials, such as sulphur or air, which, in combination with a Mg anode, possess an attractive theoretical energy density of 4508 and 14046 Wh l^{-1}, respectively.

The first non-nucleophilic electrolyte based on hexamethyldisilazide magnesium chloride (HMDSMgCl) has been reported by Kim *et al*., where the electrolyte is synthesized through several steps under strict conditions and a solution of pure crystals in THF is needed for a voltage stability of 3.2 V.[4]

This work presents a convenient route for the preparation of non-nucleophilic electrolytes based on magnesium bis-amides [$Mg(NR_2)_2$, R = $-CH(CH_3)_2$, $-Si(CH_3)_3$]. The electrolytes with an optimized composition have been characterized by means of single crystal analysis, NMR and mass spectroscopy. Such electrolytes exhibit reversible Mg deposition-dissolution characteristics with cycling efficiency > 90% and high oxidative stability up to 3.9 V. Furthermore, the feasibility of the preparation makes the *in situ* generated electrolyte practically very promising for potential high energy magnesium batteries.

References

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