

### Electrolytes for Mg-secondary batteries based on EMImCl ionic liquid, AlCl<sub>3</sub> and δ-MgCl<sub>2</sub>

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Mg-based secondary batteries are attracting candidates to satisfy the increasing demand at the global level for efficient and safe energy storage systems. Mg-based devices show intrinsic advantages in comparison with competing technologies, e.g., those based on Li. In particular, Mg is more abundant in Earth's crust in comparison to Li and suffers from fewer concerns in terms of safe use, disposal and waste management [1-3]. Mg is able to provide a larger volumetric capacity as compared to Li (3832 vs. 2062 mAh·cm<sup>-3</sup>) [4, 5]; in addition, Mg batteries have a very good cyclability, lose little capacity over prolonged cycling and have a wide temperature operation range. On the other hand, practical Mg batteries tend to show low specific energy values [6].

One of the most important obstacles to devise viable Mg-based secondary batteries is the development of electrolytes capable to transport efficiently magnesium ions without undergoing degradation, and showing a good compatibility with the electrode materials (i.e., Mg metal at the anode and oxygen- or sulfur-based systems at the cathode) [3-5]. The approach proposed in this work to address these issues is to devise electrolytes based on an ionic liquid (IL), which dissolves a suitable source of Mg ions. ILs are a promising family of candidates for this type of applications owing to their high chemical stability, low volatility and flammability, and remarkable capability to act as solvents [7].

In details, the proposed electrolytes consist of different amounts of δ-MgCl<sub>2</sub> dissolved in a homogeneous mixture of aluminum trichloride and 1-ethyl-3-methylimidazolium chloride (EMImCl) ionic liquid, and are indicated as EMImCl/(AlCl<sub>3</sub>)<sub>m</sub>/(δ-MgCl<sub>2</sub>)<sub>n</sub>. The chemical composition of the electrolytes is determined by ICP-AES and microanalysis; the samples are investigated by high-resolution thermogravimetry and modulated differential scanning calorimetry to determine the thermal stability and highlight the phase transitions; the short-range structure and interactions are elucidated by vibrational spectroscopies (e.g., FT-IR in the medium and far infrared). The electrochemical window of stability is measured, and the applicability of the EMImCl/(AlCl<sub>3</sub>)<sub>m</sub>/(δ-MgCl<sub>2</sub>)<sub>n</sub> electrolytes in prototype cells is gauged by Mg stripping/plating measurements. Finally, the electrical response of the EMImCl/(AlCl<sub>3</sub>)<sub>m</sub>/(δ-MgCl<sub>2</sub>)<sub>n</sub> electrolytes is studied in detail by broadband electrical spectroscopy (BES). The integration of all the results allows to: (a) propose a mechanism describing the long-range charge migration in the electrolytes; and (b) elucidate the complex interplay between the composition, the nanostructure and the

electrical response.

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