



Synthesis of magnesium chloride complex electrolyte: Galvanic couple assisted catalytic dissolution of magnesium in ethereal solution

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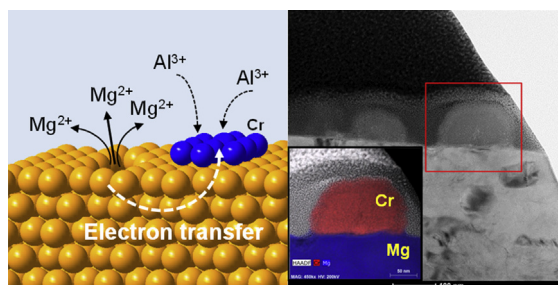
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HIGHLIGHTS

- Synthetic mechanism of MaCC electrolyte for rechargeable Mg batteries is revealed.
- Nanoscale Cr-Mg galvanic couples act as heterogeneous catalysts for Al deposition.
- First-principles calculation accounts for selective deposition of Al on Cr islands.
- Enhanced Mg dissolution by galvanic couples leads to ultrahigh Mg to Al ratio.
- Ultrahigh Mg to Al ratio explains the conditioning-free properties of MaCC.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Magnesium chloride complex
Chromium chloride
Heterogeneous catalysis
Galvanic couple
First-principles calculation

ABSTRACT

Herein, we reveal the critical role of CrCl_3 and the mechanism for the synthesis of magnesium chloride complex (MaCC), an advanced conditioning-free electrolyte for rechargeable magnesium batteries. This involves a catalytic dissolution of Mg metal by nanoscale bimetallic galvanic couples in an ethereal solution: At the initial stage, nanoscale amorphous Cr-rich ‘islands’ form on Mg surface, creating numerous Cr-Mg galvanic couples. These Cr-rich islands act as local cathodic sites due to partial electron transfer from Mg metal substrate. Furthermore, the first-principles calculation shows that Al prefers to bind at Cr-rich regions rather than Mg. These trigger a heterogeneous catalysis for the selective deposition of Al on Cr-rich islands and a dramatic increase in the dissolution rate of Mg metal on the neighboring region. This leads to an ultrahigh Mg^{2+} -to- Al^{3+} concentration ratio in the resultant solution, a key property of the conditioning-free electrolyte. This study is potentially applicable to many other fields like metal-air batteries and corrosion protection of metals, where a subtle manipulation of passive layer is required.

1. Introduction

Thanks to the low material cost, potentially high energy density, and non-dendritic character of Mg deposition, rechargeable magnesium

batteries have emerged as one of the most plausible candidates for application in mid-to-large-scale power storage devices [1–9]. To date, research has focused on the development of functional electrolytes that exhibit highly reversible characteristics for Mg deposition, high ionic

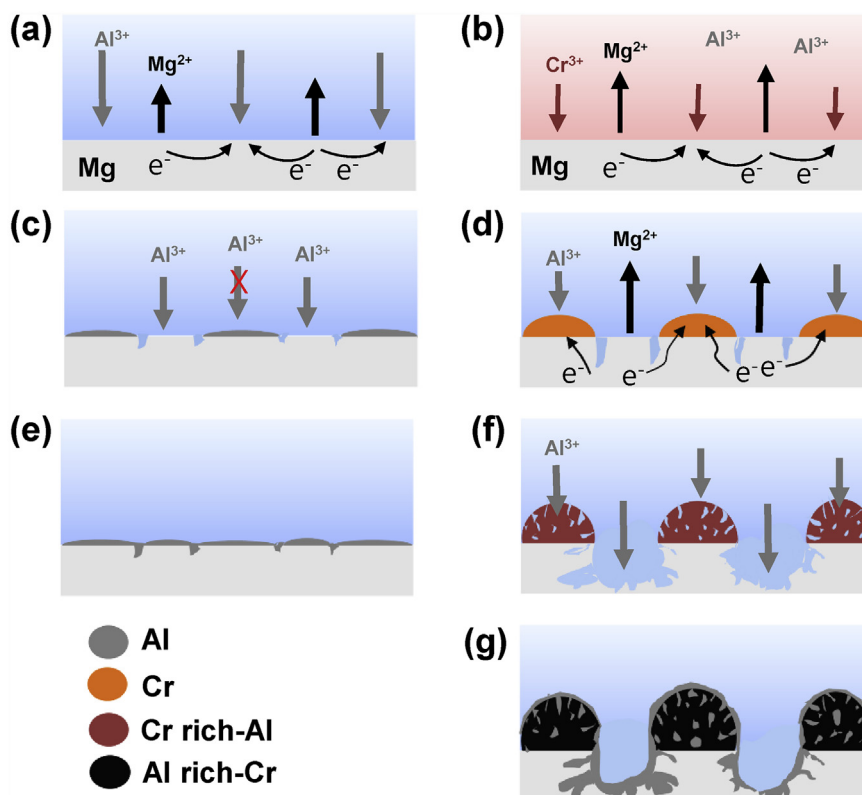
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<https://doi.org/10.1016/j.jpowsour.2018.07.058>

Received 8 May 2018; Received in revised form 2 July 2018; Accepted 14 July 2018

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Scheme 1. Schematics representing the magnesium dissolution reactions in an AlCl_3 solution with and without CrCl_3 additives; (a),(c),(e) AlCl_3 solution only and (b), (d),(f),(g) $\text{AlCl}_3/\text{CrCl}_3$ solution.

conductivity, and high oxidative stability windows [10–13]. After several decades of hard research, functional electrolytes were achieved through prudent combination of Lewis acids such as AlCl_3 and Lewis bases containing Mg^{2+} ions in etheral solvents [7,14–16].

Recently, the magnesium aluminum chloride complex (MaCC), first reported by Aurbach et al. has gained considerable attention as one of the most viable electrolyte solutions for rechargeable magnesium batteries [17]. It shows 100 % coulombic efficiency for Mg deposition-stripping and high oxidative stability up to 3.1 V versus Mg/Mg^{2+} . MaCC is prepared by simple dissolution of MgCl_2 and AlCl_3 in a 2:1 ratio in etheral solvents such as tetrahydrofuran (THF) or dimethoxyethane (DME). However, in order to become fully functional, the MaCC electrolyte requires electrolytic conditioning [18–20]. This process involves hundreds of electro-deposition/stripping cycles to achieve high coulombic efficiency. The low initial efficiency is primarily attributed to irreversible aluminum deposition on the electrode during the early cycles. This irreversible aluminum deposition is caused by the high initial concentrations of Al^{3+} in the electrolyte because it is thermodynamically more favorable than Mg [18–20].

A new MaCC-like electrolyte, called magnesium chloride complex (MaCC), was recently reported [21]. This new electrolyte is similar to MaCC in nature, but does not require cumbersome conditioning processes. The ultra-high initial $[\text{Mg}^{2+}]/[\text{Al}^{3+}]$ ratio of MaCC (~13), is much higher than that for MaCC (~2), and is speculated to enable ~100 % coulombic efficiency of the Mg deposition/stripping reaction from the first cycle. This practically important and theoretically intriguing feature originates from the unique synthesis method for MaCC, which involves a catalytic dissolution of Mg metal in a THF solution containing AlCl_3 solute. Interestingly, significant Mg dissolution is observed to proceed only when a small amount of CrCl_3 is added to the solution. However, the precise reaction mechanism and the concrete role of CrCl_3 in the synthesis of MaCC electrolyte are not yet clearly understood.

In this work, we reveal the detailed reaction mechanism of Mg dissolution in an AlCl_3 solution containing CrCl_3 . This process involves the creation of nanoscale catalysts and heterogeneous catalysis for Al reduction on the Mg surface.

2. Materials and methods

2.1. Preparation of electrolyte solutions

2.1.1. $\text{AlCl}_3/\text{CrCl}_3$ solution

In an argon-filled glove box, Anhydrous AlCl_3 (0.1333 g, Sigma-Aldrich) was slowly dissolved in inhibitor-free tetrahydrofuran (5 mL, THF, Sigma-Aldrich) in a glass bottle to obtain a clear solution. And then, CrCl_3 (0.0050 g, Sigma-Aldrich) was completely dissolved into the solution.

2.1.2. “MaCC” electrolyte

Magnesium metal powder (0.1500 g, Sigma-Aldrich Product No. 13112) was added to the $\text{AlCl}_3/\text{CrCl}_3$ solution (5 mL) and stirred for 48 h. Then, the solution was filtered with a PTFE syringe to remove any unreacted Mg metal. The collected solution was served as MaCC electrolyte [21].

2.1.3. “MaCC” electrolyte

Anhydrous AlCl_3 powder (0.1782 g) was completely dissolved in the THF solution (5 mL) and anhydrous MgCl_2 powder (0.2541 g, Sigma-Aldrich) was added and stirred for 48 h [17]. All the experiments were carried out in an argon-filled glove box (MBRAUN MB 200 B, < 0.1 ppm O_2 and H_2O) at 25 °C.

2.2. Characterization of materials

Morphological features of the deposit on Mg surface were observed

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