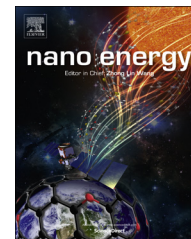




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RAPID COMMUNICATION

# Nanocomposite polymer electrolyte for rechargeable magnesium batteries



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## Abstract

Nanocomposite polymer electrolytes present new opportunities for rechargeable magnesium batteries. However, few polymer electrolytes have demonstrated reversible Mg deposition/dissolution and those that have still contain volatile liquids such as tetrahydrofuran (THF). In this work, we report a nanocomposite polymer electrolyte based on poly(ethylene oxide) (PEO), Mg(BH<sub>4</sub>)<sub>2</sub> and MgO nanoparticles for rechargeable Mg batteries. Cells with this electrolyte have a high coulombic efficiency of 98% for Mg plating/stripping and a high cycling stability. Through combined experiment-modeling investigations, a correlation between improved solvation of the salt and solvent chain length, chelation and oxygen denticity is established. Following the same trend, the nanocomposite polymer electrolyte is inferred to enhance the dissociation of the salt

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Mg(BH<sub>4</sub>)<sub>2</sub> and thus improve the electrochemical performance. The insights and design metrics thus obtained may be used in nanocomposite electrolytes for other multivalent systems.  
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## Introduction

Magnesium batteries have attracted increasing attention as a potentially low-cost, safe technology for large scale applications such as transportation and grid storage [1,2]. Magnesium—a divalent charge carrier—exhibits several intrinsic advantages for battery applications over other metals such as Li or Na. Mg metal is much less reactive in air than both Li and Na which makes it safer to handle; it has a significantly higher volumetric capacity (i.e., 3832 mAh cm<sub>Mg</sub><sup>-3</sup>, 2062 mAh cm<sub>Li</sub><sup>-3</sup> and 1136 mAh cm<sub>Na</sub><sup>-3</sup>); and smooth, dendrite-free Mg deposition [3,4] and close to a 100% coulombic efficiency (CE) for plating/stripping [5] have been demonstrated in selected electrolytes. These findings are potentially transformative since dendrite formation and low CE have been historic obstacles for Li metal battery development [6-8]. Finally, Mg is both abundant and inexpensive.

Over the past few years, extensive progress has been made in the rechargeable Mg battery field, especially with regard to electrolyte design and development [5,9-22]. Magnesium forms a “truly” passivating film in contact with oxygen or conventional electrolytes (i.e., mixtures of simple Mg salts and aprotic solvents, analogous to those in Li-ion batteries [23]), which impedes Mg<sup>2+</sup> transfer [24-26]. Hence, a rechargeable Mg battery requires electrolytes in which no “solid electrolyte interphase” (SEI) or a weakened passivation layer is formed on the Mg metal surface to enable highly reversible Mg plating/stripping [2,21,27-31]. This design metric is in contrast to Li-ion batteries in which a stable, but Li<sup>+</sup> conductive SEI is formed [32]. To date, functional electrolytes for a rechargeable Mg battery consist of complicated Mg complexes which possess a partial organometallic character [2,5,11,13,21,33]. These electrolytes usually also contain volatile solvents such as THF [2,21,34-36], which present a safety concern. The search for Mg electrolytes with solvents exhibiting higher boiling points, including ionic liquids [37,38], has been performed [39-41]. However, even though electrochemical Mg plating/stripping behavior has been reported in systems using ILs [42,43] and glymes [41], the reproducibility and truly reversible Mg plating/stripping in these systems still need to be confirmed [28,35], as large overpotentials and low CEs are observed [41,44-46].

Solid-state batteries (mostly based upon Li or Na chemistries [47-49]) provide great advantages such as flexibility in dimensions/geometry, ease of fabrication, a potentially high energy density, and most importantly high safety [49,50]. Solid-state electrolytes for battery applications can be roughly classified into two categories: inorganic and polymer-based. Recently, it has been reported [40] that a Mg(BH<sub>4</sub>)(NH<sub>2</sub>) solid-state electrolyte can enable reversible Mg plating/stripping (but with a CE of less than 50% and conductivity of 10<sup>-6</sup> S/cm at 150 °C). There is also a recent report using metal-organic frameworks as a solid Mg electrolyte, but no electrochemical data have been demonstrated [51].

Significant efforts have been devoted to polymer-based (such as poly(ethylene oxide), PEO) solid-state rechargeable Mg batteries [50,52-57]. However, most of the polymeric solid-state Mg electrolytes in the literature are based on simple Mg salts such as magnesium triflate Mg(SO<sub>3</sub>CF<sub>3</sub>)<sub>2</sub> [58] and magnesium(II) bis(trifluoromethanesulfonyl)imide Mg(N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>)<sub>2</sub> (or Mg(TFSI)<sub>2</sub>) [59], similar to those for solid-state lithium electrolytes [60]. These salts are known to be incompatible with the Mg metal anode (i.e., unable to produce reversible Mg plating/stripping) [30,35]; furthermore, it has been reported that the electrolytes based upon polymers and simple Mg salts are principally *anion conductors* (the transport number of Mg<sup>2+</sup> being very low if not zero) because of the double charge and small size of Mg<sup>2+</sup> [61-63]. There have been some efforts to increase the Mg<sup>2+</sup> transference number, but no electrochemical properties—especially those pertaining to reversible Mg plating/stripping—have been reported [64,65]. Finally, there is one interesting report on solid-state Mg polymer electrolytes, consisting of PEO or PVDF and organometallic Mg complex salts, such as Mg(AlEtBuCl<sub>2</sub>)<sub>2</sub>/THF or tetraglyme, by Aurbach and coworkers [50] demonstrating reversible Mg plating/stripping.

To the best of our knowledge, there has been no report yet on Mg polymer electrolytes without flammable plasticizers that enable reversible Mg plating/stripping. More significantly, there is little fundamental understanding available on solid-state electrolytes for rechargeable Mg batteries. In this work, we report a new nanocomposite electrolyte based on PEO-Mg(BH<sub>4</sub>)<sub>2</sub> for reversible Mg plating/stripping with a high CE and stable cycling. A design metric leading to this electrolyte chemistry has been elucidated using combined nuclear magnetic resonance (NMR) spectroscopy and theoretical molecular dynamics (MD) simulations.

## Materials and methods

### Chemicals

Magnesium borohydride (Mg(BH<sub>4</sub>)<sub>2</sub>, 95%), magnesium ribbon (99.5%), MgO nanoparticles, polyethylene oxide (PEO, MW 600,000), and anhydrous tetrahydrofuran (THF) were purchased from Sigma-Aldrich. Magnesium bis(trifluoromethylsulfonyl)imide (Mg(TFSI)<sub>2</sub>) was purchased from SOLVIONIC (France). Battery grade dimethoxyethane (DME), diglyme, triglyme, tetraglyme were obtained from Novolyte Technologies, Inc. The solvents were further dried over 3 Å molecular sieve, PEO was dried under vacuum at 60 °C for 24 h, and MgO nanoparticles were dried under vacuum at 300 °C for 24 h before use.

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