



Electrochemical performance and redox mechanism of naphthalene-hydrazine diimide polymer as a cathode in magnesium battery

Tanja Bančič^{a,b}, Jan Bitenc^a, Klemen Pirnat^a, Anja Kopač Lautar^a, Jože Grdadolnik^a, Anna Randon Vitanova^c, Robert Dominko^{a,b,d,*}

^a National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia

^b Faculty of Chemistry and Chemical Technology, University of Ljubljana, Večna pot 113, 1000 Ljubljana, Slovenia

^c Honda R&D Europe GmbH, Carl-Legien Strasse 30, 63703 Offenbach, Germany

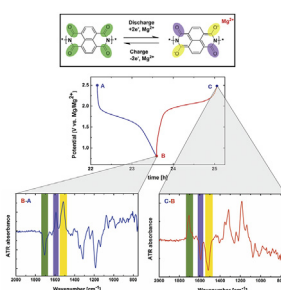
^d Alistore ERI, Amiens, France



HIGHLIGHTS

- Naphthalene-hydrazine diimide polymer (NP) can perform as a cathode material in Mg batteries.
- Electrochemical performance of NP depends on used electrolyte.
- Redox mechanism of NP is determined through *in operando* ATR IR spectroscopy.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Batteries
Electrochemistry
Energy storage
Magnesium
Polymers

ABSTRACT

A magnesium (Mg) battery in the combination with the redox active polymers possesses attractive electrochemical properties as a future battery technology. This concept has been demonstrated by using quinone based polymers and the non-nucleophilic electrolytes, while polyimides were rarely investigated. In this work, a naphthalene-hydrazine diimide polymer (NP) has been tested as a cathode material for Mg organic battery in two different electrolytes. Average discharge voltage of the Mg-NP battery is 1.70 V with Coulombic efficiency above 99% in the TEGDME/DOL based electrolyte. The electrochemical mechanism was studied by *in operando* ATR IR spectroscopy and confirmed by DFT calculation of the IR spectra. We confirmed redox activity of carbonyl moieties, which undergo reversible reduction to enolate anion. Moreover, *in operando* IR spectroscopy shows charge delocalization in the reduced form since none of the bonds has pure single/double bond character.

1. Introduction

Modern age has brought a great development in many aspects of human life. Constantly expanding industry is connected with a growing increase of energy demand. We are facing important sustainability challenges that require a game-changing approach in searching new, environmentally acceptable solutions to existing energy problems. For

the same reason development of novel, more sustainable battery technologies, that could replace currently prevalent lithium-ion (Li-ion) technology, has begun to receive more attention. The goals are higher energy density, improved safety and use of environmentally benign, recyclable components. Promising candidates to fit those demands are magnesium (Mg) secondary batteries with Mg metal anode. In comparison with Li, Mg batteries exhibit several attributes such as higher

* Corresponding author. National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia.
E-mail address: robert.dominko@ki.si (R. Dominko).

volumetric capacity (3832 mAh cm^{-3} vs. 2046 cm^{-3} for Li), wide availability in Earth's crust (and consequently notably lower cost), improved safety properties due to reduced reactivity towards air and water, as well as low reduction potential (-2.37 V vs. SHE, only 0.67 V higher than Li). Although the reversible stripping and deposition of Mg was first demonstrated by Gregory and coworkers in 1990 [1] and first example of secondary Mg battery was published by Aurbach and coworkers in 2000 [2], we are still lacking suitable cathode compounds, which would result into a commercially interesting system. Another challenge of Mg batteries is compatibility of Mg metal with different electrolytes. Desired properties of the electrolyte are high oxidative stability ($> 3.5 \text{ V}$ vs. Mg), limited corrosion of non-noble metals, low overpotentials ($< 100 \text{ mV}$) for the deposition of Mg, high conductivities ($> 10 \text{ mS/cm}$), and simple synthesis and purification. Up-to-date, all of these demands have not yet been met by a single electrolyte at least to some extent [3].

Insertion cathode materials, traditionally used in the Li-ion batteries (transition metal-based inorganic materials), have issues with adoption in Mg batteries. The kinetics of solid state diffusion of Mg^{2+} ion through inorganic cathode materials is very slow, resulting in low capacities, low operating voltages and low current capabilities [4]. Solid state diffusion limitations are overcome in organic materials as redox sites are much easier accessible to ions.

Organic cathode materials represent more versatile, inexpensive and environment friendly alternative as their synthesis is much less energy intensive and can be relatively easily adjusted to obtain structurally diverse candidates. With minimal structure modifications we can obtain desired properties such as redox potential [5], electronic conductivity [6], capacity stability [7], and physical properties [8]. Another asset is possible use of the same material with different anodes. Counter-ions' interaction with the electrode is not based on intercalation and thus ion radii is not playing a crucial role [4]. Great example of activity with various cations is PHBQS (poly(hydroquinonyl-benzoquinonyl sulfide)), which shows excellent electrochemical activity in Li and Mg batteries [9].

There have been several reports about reversible redox activity of organic molecules in Li batteries, the best results typically displayed by conjugated carbonyl-based polymers [10,11]. Their advantages are fast reaction kinetics, good reversibility and structural diversity. Among conjugated carbonyl polymers, aromatic polyimides represent a promising class of redox-active electrode materials for energy storage applications. They are decorated by high thermal stability and mechanical strength [12], both of them being desired properties also for organic cathode materials. Generally they are synthesized by polycondensation between aromatic dianhydride and diamine. Ideally, each polyimide unit with four carbonyl groups would transfer four electrons during redox reaction. In practice, only two one-electron steps are reversible and thus useful for charge storage [13]. Their electrochemical activity has been demonstrated in lithium organic batteries [13–18]. On the other hand, only a few papers show electrochemical characterization of organic cathodes in Mg batteries [9,17–21], with a single report where polyimides are tested as an anode in the combination with Prussian blue as a cathode in an aqueous electrolyte [22].

In this work, we report reversible behavior of polyimide naphthalene-hydrazine diimide polymer (NP) in Mg battery using two different types of non-nucleophilic electrolytes and propose the electrochemical mechanism by using *in operando* ATR IR (attenuated total reflection infrared) spectroscopy and DFT (density functional theory) calculations.

2. Experimental

2.1. Materials

Naphthalene-hydrazine diimide polymer (NP) was synthesized according to the previously reported two-step procedure [23] through

copolymerization of 1,4,5,8-naphthalenetetracarboxylic dianhydride and hydrazine at $220 \text{ }^\circ\text{C}$ (Fig. S1). General experimental details and characterization data are included in the Supporting Information.

Cathode composite in a form of a free-standing electrode consisted of NP, Printex XE2 conductive carbon and PTFE binder (mass ratio 60:30:10, respectively). All components were ball milled for 30 min at 300 rpm in suspension of isopropyl alcohol. As-prepared cathode composite was hand-rolled into thin electrodes with diameter of 12 mm and approximate NP loading of 4 mg per cm^2 . Electrodes were dried overnight at $80 \text{ }^\circ\text{C}$ prior use. Cathode composite Printex XE2 and PTFE binder was prepared using same procedure as described above. Mg powder (Alfa Aesar; 99.8%, 325 mesh) was ball milled in Ar atmosphere for 30 min at 300 rpm with 5 wt.% MgCl_2 (Alfa Aesar; 99.99%, ultra dry) and used as an anode.

Electrolyte: magnesium(II) bis(trifluoromethanesulfonyl)imide ($\text{Mg}(\text{TFSI})_2$, 99.5%) was purchased from Solvionic and dried at $120 \text{ }^\circ\text{C}$ under vacuum for 2 days. Tetraethylene glycol dimethyl ether (TEGDME, 99%) was purchased from Acros, 1,3-dioxolane (DOL, 99.8%) was purchased from Sigma. All solvents for electrolytes were dried over molecular sieves (4 \AA) up to $< 5 \text{ ppm}$ of water, then refluxed for 1 day with Na/K alloy in Ar-filled glovebox, followed by distillation under reduced pressure (5 mBar). After all the procedures the amount of water in solvents was estimated $< 1 \text{ ppm}$ by Karl Fischer titration.

2.2. Electrochemical and spectroscopic measurements

All electrochemical cells were assembled in Ar-filled glovebox with water and oxygen content below 1 ppm. Details about electrochemical characterization in Li batteries are provided in the Supporting Information file.

Electrochemical characterizations were conducted on Bio-Logic VMP3 potentiostat and were performed in two-electrode Swagelok[®] laboratory cell with graphite discs as cathode current collectors and GF/A Whatman glass fiber as a separator. *In operando* ATR IR measurements were performed in a modified pouch cell (Fig. S9, details described in Supporting Information).

ATR IR measurements were conducted on Bruker Vertex 80 with a liquid nitrogen cooled mercury cadmium telluride (MCT) detector and equipped with a Specac Silver gate ATR with germanium (Ge) crystal. The ATR IR spectra were collected every 3 min in absorbance mode with 64 scans at a resolution of 4 cm^{-1} in the range of $4000\text{--}500 \text{ cm}^{-1}$. The automatic baseline correction and atmospheric compensation were performed on the ATR IR spectra in OPUS version 7.0 software.

All calculations were performed by Gaussian 09 software [27] using M06-2X hybrid functional of Truhlar and Zhao [28], and the 6-31 + G(d,p) basis set. Polarizable continuum model with a dielectric constant of 7.6 was used to simulate surrounding medium and three monomeric units as a model a polymeric structure of NP (Fig. S8). IR analysis was performed without modes involving contributions from terminal groups and with a scale factor of 0.95 [29,30].

3. Results and discussion

NP was synthesized as described in the literature [23] by a two-step reaction (Fig. S1a) between anhydride and diamine, followed by polycondensation. IR spectra shown in Fig. S1b is in the agreement with published data [23]. Two electrolytes were used for galvanostatic electrochemical tests, both containing 0.4 M magnesium(II) bis(trifluoromethanesulfonyl)imide ($\text{Mg}(\text{TFSI})_2$) and 0.4 M MgCl_2 in a solvent, one being a mixture of tetraethylene glycol dimethyl ether (TEGDME) and 1,3-dioxolane (DOL) in ratio 1:1, v/v % and the other electrolyte containing pure TEGDME as a solvent. In the first discharge, the capacity obtained was 23% of theoretic capacity ($C_{\text{theor}} = 203 \text{ mAh g}^{-1}$ for two electrons per monomer unit). This is fairly low compared to the capacity measured in the Li battery, where capacity close to the theoretical value has been obtained (Fig. S2). Reasons for lower

Download English Version:

<https://daneshyari.com/en/article/7724760>

Download Persian Version:

<https://daneshyari.com/article/7724760>

[Daneshyari.com](https://daneshyari.com)