



Review

Cathode materials for magnesium and magnesium-ion based batteries



Matthew M. Huie^a, David C. Bock^b, Esther S. Takeuchi^{a,b,c},
Amy C. Marschilok^{a,b}, Kenneth J. Takeuchi^{a,b,*}

^a Department of Materials Science and Engineering, Stony Brook University, Stony Brook, NY 11794, United States

^b Department of Chemistry, Stony Brook University, Stony Brook, NY 11794, United States

^c Brookhaven National Laboratory, Upton, NY 11973, United States

Contents

1. Introduction	15
2. Cathode materials	16
2.1. Vanadium oxide	16
2.2. Prussian blue analogs	19
2.3. Molybdenum sulfide	19
2.3.1. Chevrel phase: Mo ₆ T ₈ where T = S or Se	19
2.3.2. Molybdenum disulfide MoS ₂	20
2.4. Molybdenum oxide	20
2.5. Manganese oxides	21
2.5.1. Tunneled MnO ₂ (hollandite and todorkite)	21
2.5.2. Layered MnO ₂ (birnessite)	22
2.5.3. Spinel MnO ₂	22
2.5.4. Post-spinel MnO ₂	23
2.6. Transition metal silicates	24
2.7. Other cathode materials	25
3. Conclusions	26
Acknowledgement	26
References	26

ARTICLE INFO

Article history:

Received 9 September 2014

Accepted 19 November 2014

Available online 24 December 2014

Keywords:

Magnesium battery
Magnesium-ion battery
Energy storage
Cathode material

ABSTRACT

Rechargeable magnesium-ion batteries are a promising candidate technology to address future electrical energy storage needs of large scale mobile and stationary devices, due to the high environmental abundance of magnesium metal and divalent character of magnesium ion. With the recent increase in reports discussing cathode materials for magnesium-ion batteries, it is instructive to assess recent research in order to provide inspiration for future research. This review is a summary of the different chemistries and structures of the materials developed for magnesium ion cathodes. The particular strategies which may lead to future research initiatives are amplified.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

The efficient management of energy sources, both renewable and non-renewable, on local and large bases, is critical to addressing important global issues such as energy demand,

fossil fuels economies and limitations, and human induced climate change. Crucial to the efficient management of energy sources are batteries of various performance profiles which can store and release generated electrical energy at levels appropriate for a number of application power demands. For example, the development of electric vehicles, as well as the growing electrical energy storage needs of mobile and stationary devices demonstrate the need for rechargeable batteries with a variety of application-based performance capabilities, including sufficient energy density, appropriate voltage and current capabilities, and the safe management of heat.

* Corresponding author at: Department of Chemistry, Stony Brook University, Stony Brook, NY 11794, United States. Tel.: +1 6316328579.

E-mail address: kenneth.takeuchi.1@stonybrook.edu (K.J. Takeuchi).

Table 1
Comparison of characteristics of magnesium (Mg) and lithium (Li).

Characteristics	Mg	Li	References
Pauling Ionic Radius	65	60	[3]
Voltage vs. S.H.E.	−2.37	−3.04	[2]
Elemental abundance (ppm in earth's crust)	2.33E+04	2.00E+01	[5]
Volumetric capacity (mAh/cm ³)	3833	2046	[6]
Gravimetric capacity (mAh/g)	2205	3862	[4]

Another critical issue in battery development is cost. One of the most successful and broadly implemented rechargeable battery technologies developed to date is lithium ion. However, questions regarding the future of using lithium ion technology for large scale applications center on the sustainability and high cost of lithium, especially due to the projected increase in demand for lithium based electrodes used in hybrid and plug in electric vehicles and stationary (grid) storage [1–3]. It is projected that costs may continue to rise as these new technologies gain a greater share of the market, and new lithium reserves will be needed to keep up with demand [3].

Of the possible alternatives to lithium-ion, rechargeable magnesium-ion batteries are a promising candidate, and research into the technology has accelerated in recent years (Fig. 1).

Magnesium-ion technology is promising for several reasons. First, due to the natural abundance of magnesium in the earth's crust, approximately 10⁴ times that of lithium, its incorporation into electrode materials is inexpensive (Table 1). Secondly, magnesium is more atmosphere stable and has a higher melting point than lithium, making it safer relative to lithium [4]. The divalent nature of magnesium ions also presents a potential advantage in terms of volumetric capacity (3833 mAh/cm³ for Mg vs. 2046 mAh/cm³ for Li).

Despite these positive attributes, the development of magnesium-ion technology has not kept pace with that of lithium ion technology. One critical issue impeding progress has been development of a suitable electrolyte which will enable reversible release of Mg²⁺ ions from a magnesium metal anode [7]. Unlike Li⁺ ion conducting surface films formed by polar aprotic electrolyte solutions on Li metal electrodes, surface films on magnesium metal often block the transport of Mg²⁺ ions [8]. For example, the use of magnesium salts such as Mg(ClO₄)₂ and Mg(BF₄)₂ paired with organic solvents such as carbonates or nitriles results in the formation of surface films which passivate the magnesium metal electrode [8]. Thus, the use of magnesium based electrolytes which are analogous to those commonly used with Li⁺ ion technology is not ideal. Notably, an advancement in this area was reported in 2000 with the development of electrolyte based on magnesium organo-haloaluminate complexes dissolved in tetrahydrofuran (THF) or glyme based solvents [9]. These electrolytes allow for electrochemical deposition–dissolution of magnesium and have a stable electrochemical window of 2.5 V, thereby allowing for the testing of practical cathode materials. However, the magnesium haloaluminate complexes are corrosive and reactive, particularly with water, causing additional constraints in terms of the necessary stabilities of the cell components.

A second ongoing challenge is the development of cathode materials which have high reversible capacity and adequate operating voltage under appropriate power output conditions. Due to the high valency of Mg²⁺ ions, the kinetics of solid state diffusion through inorganic cathode materials is slow, resulting in low reversible capacity and reduced power output. Recent work suggests that low Mg²⁺ mobility is caused by both strong ionic interactions as well as redistribution of the divalently charged

cations in the host material [10]. To address these issues, several strategies have been reported. For example, mesoporous and nanostructured materials [11] which display large surface areas have been employed as electrode materials in order to decrease the diffusion length for Mg²⁺ ions into host cathode sites. Further, the use of materials with high divalent ion mobility [12,13] have been used as electrode materials in order to increase current capabilities.

With the recent increase in reports involving cathode materials for magnesium-ion batteries, it is important to assess recent research in order to provide inspiration for future research. Specifically, there are many magnesium-ion studies involving numerous cathode compositions and various phases (Table 2). In the past five years there have been several reviews written about magnesium-ion batteries [4,6,13]. The goal of this review is to augment the previous literature in this field by focusing on structure–function relationships of various classes of cathode materials in the context of their coordination chemistry. By summarizing the electrochemical performance in magnesium based systems in light of the known structures which function most effectively as magnesium ion cathodes, we hope to reveal particular strategies which may facilitate future developments in this field.

2. Cathode materials

2.1. Vanadium oxide

Crystalline V₂O₅ consists of layers of V₂O₅-based polyhedra, which provides pathways for ion insertion and removal (Fig. 2). A screening of metal-oxides and metal-sulfides to determine Mg²⁺ reversibility indicated that V₂O₅ had an open circuit voltage of 2.66 V, the second highest voltage of all the screened compounds when paired with magnesium foil in 1.0 M Mg(ClO₄)₂ in THF. Notably, the highest open-circuit voltage belonged to lead-oxide compounds; however the large density of lead results in low gravimetric energy density.

Intercalation of Mg²⁺ into V₂O₅ is a slow process, possibly due to chemical modification of the V₂O₅ crystal surface [7]. Further, V₂O₅ electric conductivity is low. To optimize the diffusional pathways of Mg²⁺ during the charging and discharging of V₂O₅, reports have appeared involving the control of crystallite size [14,22–24] and the use of conductive additives [19,20]. Decreasing crystallite size decreases the diffusion path length within the V₂O₅ crystals, improving capacity at higher current rates. This strategy has been utilized in work which investigates nanocrystalline V₂O₅ [14] and V₂O₅ nanotubes [22–24], although more work needs to be completed to compare the electrochemistry of the nanocrystalline materials with microcrystalline V₂O₅ in order to accurately assess the effectiveness of this approach. The use of conductive materials has also been tested as a means of improving Mg²⁺ diffusion. When the electrochemical performance of a composite carbon – V₂O₅ xerogel consisting of aggregated acetylene black carbon particles covered with a thin layer (<100 nm) of V₂O₅ xerogel was compared to that of an electrode prepared via a conventional mixture of V₂O₅, the composite exhibited higher capacity [19,20]. This improvement was attributed to shorter diffusion length of Mg²⁺ through the thin V₂O₅ layer in the composite.

Vanadium oxide gels (V₂O₅·*n*H₂O) have crystal structures comprised of layered square-pyramidal VO₅ polyhedra in which V⁵⁺ is coordinated with five oxygen atoms. Water molecules are bound between the layers of V₂O₅. The layered structure allows V₂O₅ to cleave along the layers, but also provides channels for ion insertion and deinsertion. A critical aspect in the research of V₂O₅ cathodes is water content, because water in the electrolyte can solvate and partially shield the divalent magnesium-ion charge, allowing for easier insertion and deinsertion into the crystal. Notably, desolvation

Download English Version:

<https://daneshyari.com/en/article/1299847>

Download Persian Version:

<https://daneshyari.com/article/1299847>

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