Rechargeable Magnesium Batteries Based on Phosphonate Electrolytes

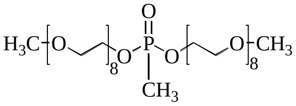
Brian G. Dixon
Massachusetts Maritime Academy
Buzzards Bay, MA
&
Phoenix Innovation, Inc. Sandwich, MA

R. Scott Morris
Brett Gall
Phoenix Innovation, Inc. Sandwich, MA

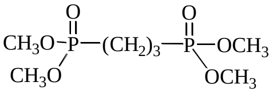
Magnesium electrochemical systems have not received the attention their promise justifies.[1] To date the majority of work involving magnesium has revolved around the use of electrolyte materials, such as Grignard reagents, that present the same set of safety and instability problems typical with lithium. In this case there would be no advantage to using magnesium. Although magnesium runs at a substantially lower voltage than lithium, the metal is inherently safer. Lithium batteries are clearly the focus of a great deal of research and commercial develop. The high reactivity of lithium requires non-aqueous, aprotic electrolytes in order to preclude undesirable side reactions of lithium, and to control its explosive nature. In instances of abuse, reactive liquid electrolyte products have been implicated as a source of explosions in secondary lithium batteries.

Successful development of alternative, complimentary, electrochemical systems would afford greater flexibility to battery system developers and consumers. In this regard, magnesium is an attractive anode material because of its high charge density (low electrochemical equivalence) and negative electrode potential (-2.37V vs. NHE). Magnesium primary batteries are well known, but its use in secondary cells has been stymied by the lack of suitable non-aqueous electrolyte that can conduct Mg^{+2} species, combined with poor stripping and plating properties

We have been exploring a family of non-flammable phosphonate electrolyte solvents, two of which are shown below. Their preparations are contained in the supplementary material.



a



b

Electrolytes were formulated from these two solvents using either magnesium triflate (MgTf) or magnesium trifluoromethane-sulfonimide (MgIm) as the conductive salt.

Electrochemical Results

Table 1 compares the ionic conductivities of our phosphorous containing electrolytes with those prepared with traditional CH_3O-capped polyethyleneglycol (PEG) solvents. Ionic conductivity of the magnesium electrolytes was determined with one of three commercially available magnesium salts, MgIm, MgTf, and magnesium perchlorate at room temperature using typical impedance procedures.

---

[1] Aurbach, D.; et al., *J. Power Sources* 2001 *97* 28.; Novak, P.; et al., *Elec. Acta* 1999 *45* 351; Yoshimoto, N.; et al., *Elec. Acta* 2003 *48* 2317; Oh, J-S.; et al., *Elec. Acta* 2004 *50* 898.

Table 1: Ionic Conductivity of Magnesium Electrolytes @ 20°C

Solvent	*Salt*	*(S/cm)*
a	0.25M $Mg(CF_3SO_3)_2$	6.0×10^{-4}
b	0.25M $Mg(CF_3SO_3)_2$	4.4×10^{-3}
a	0.25M $Mg(ClO_4)_2$	9.3×10^{-4}
a	0.25M $Mg([CF_3SO_2]_2N)_2$	7.4×10^{-4}
Dibutyl glyme	0.25M $Mg(CF_3SO_3)_2$	2.0×10^{-8}
PEG-dimethyl ether*	0.25M $Mg(CF_3SO_3)_2$	1.3×10^{-4}

* M_n ~750

As shown in Table 1, the new phosphorous based solvents yielded substantially higher conductivities than the control, and an ability to obtain higher levels of dissolved salt was also observed. Table entry #2, for the **b** liquid phosphorous containing solvent, consistently had the highest ionic conductivities with values in excess of 4 $x10^{-3}$ S/cm. These are outstanding conductivities at 20°C.

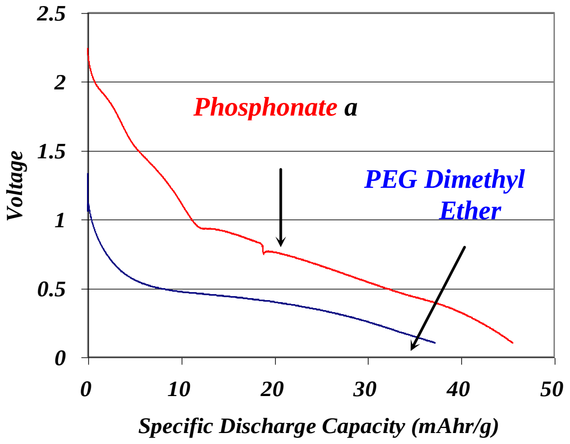
Phosphonate **a** , a bis-PEG derivative, showed little variation in conductivity with Mg salt type. The ionic conductivities of the phosphonate based electrolytes were found to be 5-10 times that of the classical methoxy end-capped PEG electrolyte solvent. Finally, the penultimate table entry, based on a glyme solvent, was poorer in ionic conductivity by 4-5 orders of magnitude.

Electrochemical Characterizations

A number of cathodes have been evaluated, of which vanadium oxide (V_2O_5) gave the best results. Electrolytes were evaluated by several electrochemical techniques including cyclic voltammetry and cell testing under constant current conditions. Presented below are results from Mg/V_2O_5 cell testing using our poly(oxyether)phosphonate electrolytes with three commercial magnesium salts and a polymer electrolyte using a commercial PEG dimethyl ether (MW 350) serving as control. For these experiments, the cells were cycled at a constant current of 0.05 mA for both discharge and charge with 0.1 V discharge and 4.0 Volt charge cutoffs. In cycling experiments, cells completed three discharges.

Figure 1 shows the first discharge curves of two cells using Mg/V_2O_5 with a 0.25 M MgTf- PEG electrolyte and a 0.25 M MgTf-poly(oxyether)phosphonate, structure **a**, electrolyte. The cell using the latter delivered both a higher specific capacity and a higher operating voltage than the cell using the PEG electrolyte.

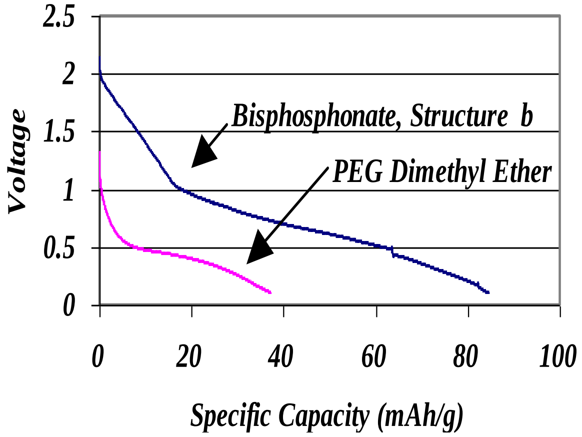
Figure 1: 1st Discharge Comparison Phosphonate a vs. PEG Dimethyl Ether[1]



1. V_2O_5/C/PVDF cathode, Mg anode, MgIm salt (1M), 22°C

We also have tested a new phosphonate electrolyte based upon structure **b** that was cycled a modest four times before cell failure, but exhibited close to 100 mAh/g initial capacity for a Mg/V_2O_5 cell (Figure 2). This run was made using an electrolyte containing 0.5M MgIm as the supporting salt yielded an ionic conductivity of 4.4 $\times 10^{-3}$ S/cm and an OCV of 2.15V.

Figure 2: 1st Discharge Mg/V_2O_5 Cells: PEG Dimethyl Ether vs Bisphosphonate b*



** structure b phosphonate solvent, V_2O_5/C/PVDF cathode, Mg anode, MgIm salt (1M), 22^oC*

Conclusions

This communication identifies a promising line of research into magnesium battery systems based upon new electrolyte solvents. These electrolytes are nonflammable polyphosphonates that have inherently high conductivities, and allow cycling (plating-stripping) of magnesium, a notoriously difiicult task. The systems use vanadium oxide cathodes whose intercalation chemistry can be adjusted to maximize the magnesium loadings. In addition, the various components can be handled and assembled in less than rigorously dry and oxygen-free conditions a substantial advantage over lithium batteries.

Our research is continuing into magnesium wherein the cycling behaviour and rechargeable voltage/ capacities are substantially improved.

Acknowledgments

The authors gratefully acknowledge the financial support of the Department of Energy under the auspices of grant #DE-FG02-04ER84040.

Supplementary Information

The phosphonates described were prepared in a single step using either a classical Arbuzov reaction or transesterification of phosphonate esters. Purifications involved simple column chromatography with commodity low cost media, such as silica, and solvents. Stainless steel blocking electrodes were used in a simple two electrode polypropylene test cell. A 0.018cm thick non-woven glass material (Hollingworth and Vose Walpole, MA) comprised the separator, which was completely wetted with the individual test electrolytes prior to the determination. Three commercially available magnesium salts, magnesium trifluoromethanesulfonimide (Mg imide, (Covalent Associates Woburn, MA.), magnesium trifluoromethanesulfonate (Mg triflate, Aldrich), and magnesium perchlorate (Aldrich) were evaluated. Electrolytes were evaluated by several electrochemical techniques including cyclic voltammetry, chronamperometry and cell testing under constant current conditions using standard procedures (Fritz, H.P.; Kuhn,. A.; *J. Power Sources* 1993 *41*, 253). The cells were cycled at a constant current of 0.05 mA for both discharge and charge with 0.1 V discharge and 4.0 Volt charge cutoffs. In cycling experiments, cells completed at least three discharges.