

Electrochemical Stability and Speciation of a Magnesocene / THF Electrolyte

Piotr Jankowski^{a,b}, Rainer Schwarz^c, Reza Younesi^d, Anna Randon-Vitanova^e,
Patrik Johansson^a, and Mario Wachtler^{c,d}

^a *Chalmers University of Technology, Department of Physics, Göteborg, Sweden*

^b *Warsaw University of Technology, Faculty of Chemistry, Warsaw, Poland*

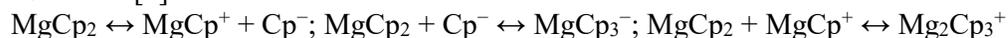
^c *ZSW – Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg, Ulm, Germany*

^d *Uppsala University, Department of Chemistry – Ångström Laboratory, Uppsala, Sweden*

^e *Honda R&D Europe (Deutschland) GmbH, Offenbach am Main, Germany*

E-mail: mario.wachtler@kemi.uu.se

Recently, bis(cyclopentadienyl)magnesium (magnesocene, MgCp₂) in tetrahydrofuran (THF) has been introduced as a new chlorine-free electrolyte for low-voltage Mg batteries [1]. Unlike ferrocene, magnesocene behaves as a weak electrolyte and shows some minor dissociation in electron-donating solvents, thus exhibiting low conductivities in the order of 10⁻⁵ S/cm [2]:



Despite the low conductivity, high Mg plating / stripping current densities can be observed, which are comparable to those of other Mg electrolytes, such as Mg(BH₄)₂ / THF [1]. The plating / stripping process shows high reversibility for many cycles, which suggests that the Mg metal anode is not overly passivated in the MgCp₂-based electrolyte. X-ray photoelectron spectroscopy (XPS) characterization of the surface of the cycled Mg electrode does not reveal any significant amounts of decomposition products or passivation films, and indicates that the electrolyte is rather stable at the working potential of the Mg metal electrode. The anodic stability has been investigated by linear sweep voltammetry, and values of approx. 1.5, 1.7, and 1.8 V vs. Mg²⁺/Mg⁰ have been observed on Pt, Cu, and stainless steel, respectively.

The experimental findings are corroborated by density functional theory (DFT) calculations performed for various hypothetical Mg-Cp-THF species, using implicit (C-PCM) THF solvation. The cathodic stability of these species is well below 0 V vs. Mg²⁺/Mg⁰, indicating that they should not be reduced at the potentials of the Mg plating / stripping reactions. The overall anodic stability of the electrolyte is limited by the Cp⁻ species, which is oxidized at 1.86 V vs. Mg²⁺/Mg⁰. The DFT calculations, furthermore, show MgCp₂THF₂ to be the most stable neutral species, wherein one Cp moiety is η⁵-coordinated, the other one is η¹-coordinated, and the THF molecules are coordinated via their oxygen atoms. The structure previously resolved for solid MgCp₂THF₂ crystals by X-ray diffraction [3] is thus preserved in THF solution.

Acknowledgements:

PJ and PJ acknowledge the support from Honda R&D Europe and several of Chalmers Areas of Advance: Materials Science, Energy and Transport. RS and MW acknowledge the financial support from the German Federal Ministry of Education and Research (BMBF) (project “Mg-Air”, 03EK3027C). RY acknowledges the support from the Swedish Government (Swedish Strategic Research Programme “STandUP for Energy”).

References:

- [1] R. Schwarz, M. Pejic, P. Fischer, M. Marinaro, L. Jörissen, M. Wachtler, *Angew. Chem. Int. Ed.* 55 (2016) 14958-14962.
- [2] W. Strohmeier, F. Seifert, H. Landsfeld, *Z. Elektrochem.* 66 (1962) 312-316.
- [3] A. Jaenschke, J. Paap, U. Behrens, *Organometallics* 22 (2003) 1167-1169.