

Thermodynamic and electrochemical properties of aqueous magnesium salt molecular crowding-based electrolytes to be used in energy storage devices.

Bénédicte Claude-Montigny^{1,*}, Carine Maaliki¹, Malaurie Paillot², Sophie Le Caër², Magali Gauthier²

¹ *Laboratoire de Physico-Chimie des Matériaux et des Electrolytes pour l'Energie (EA 6299), Université de Tours, Parc de Grandmont, F-37200, France*

² *NIMBE, CEA, CNRS, Université Paris-Saclay, CEA Saclay, 91191 Gif sur Yvette Cedex, France*

**benedicte.montigny@univ-tours.fr*

Over the past decades, many researchers have been interested in the development of aqueous electrolytes as a solution to the safety, cost and environmental problems of lithium-ion batteries or organic solvent-based supercapacitors¹⁻⁶.

In this context, aqueous electrolytes based on multivalent ions in the form of magnesium salt have attracted our attention. The main advantages of using magnesium are its really low cost, high abundance on earth (2.3 wt% in the earth's crust vs. 20-70 ppm for Li)^{7,8} and higher safety compared to Li⁹. Mg has a relatively low reduction potential (-2.4 V vs. NHE), i.e. 600 mV higher than lithium (-3 V vs. NHE)⁵, and attractive capacities in metallic form, in particular a higher volumetric capacity (3833 mAh cm⁻³_{Mg}) than Li (2062 mAh cm⁻³_{Li}). However, Mg²⁺ ions interact strongly with the electrode materials, reducing ionic conductivity and solid-state diffusion, and consequently limiting cycling stability and rate capability.

To overcome the limited voltage window using an aqueous system, we design innovative and unconventional molecular crowding electrolytes, where the presence of water-soluble polymers or molecules can alter the hydrogen bonding in water¹⁰. Based on a bio-inspired concept, an aqueous magnesium nitrate-based electrolyte is presented here using additives as water-soluble biopolymers, with strong solvating ability for Mg²⁺ ions.

From physicochemical characterisations to preliminary electrochemical studies, we show how the presence of the bio-sourced building block (from monomer to polymer) versus the magnesium cation and water molecules affects the organisation in solution, or what its influence is.

Acknowledgements

This work was supported by the French National Research Agency (ANR) under the Project ANR-21-CE50-0005-01.

References

- 1 D. Aurbach, Z. Lu, A. Schechter, Y. Gofer, H. Gizbar, R. Turgeman, Y. Cohen, M. Moshkovich, E. Levi, *Nature*, 2000, **407**, 724-727
2. A. Ponrouch, C. Frontera, F. Bardé, M. R. Palacín, *Nat. Mater.*, 2016, **15**, 169-172
3. A. Ponrouch, J. Bitenc, R. Dominko, N. Lindahl, P. Johansson, M. R. Palacin, *Energy Storage Mater.*, 2019, **20**, 253-262
4. J. Muldoon, C. B. Bucur, T. Gregory, *Chem. Rev.*, 2014, **114**, 11683-11720
5. R. Mohtadi and F. Mizuno, *Beilstein J. Nanotechnol.*, 2014, **5**, 1291-1311
6. K. Periyapperuma, T. T. Tran, M. I. Purcell, M. N. Obrovac, *Electrochim. Acta*, 2015, **165**, 162-165
7. <https://www.science.co.il/elements/>, (assessed October 2020)
8. C. W. Kamienski, D. P. McDonald, M. W. Stark, J. R. Papcun, in *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, Inc., 2000.
9. P. Canepa, G. Sai Gautam, D.C. Hannah, R. Malik, M. Liu, K.G. Gallagher, K.A. Persson, G. Ceder, , *Chem. Rev.* 2017, **117**, 4287-4341
10. J. Xie, Z. Liang, Y.-C. Lu, *Nat. Mater.*, 2020, **19**, 1006-1011