

ENERGY STORAGE AND THE METAL ELECTRODE

Michel Armand^{a,b,c},

^a CIC Energigune, C/Albert Einstein 48 Ed. Miñano, Alava 01510 (Spain)

^b LRCS, CNRS UMR 7314, Université de Picardie Jules Verne,
33 rue Saint Leu, 80039, Amiens (France)

^c Institute for Frontier Materials Deakin University, Victoria (Australia)

email address: michel.armand@gmail.com

Lithium had been identified already in the 50's as an electrode leading to high capacities and voltages, but this was in primary primary cells and the positive electrodes (e.g. AgCl) were working on a phase change reaction, far from reversible.

The change came in the early 70's with the ushering of the concept of intercalation, giving in principle an immortal electrode without new phase nucleation ^[1]. In the same decade, the Li^o/TiS₂ battery consecrated the principle ^[2]. However, this metallic lithium electrode system with liquid electrolytes was a dangerous failure, so was the subsequent Li^o/MoS₂ batteries rapidly withdrawn from market. Thus, the “rocking chair” concept whose name evolved into “lithium-ion”, known since 1978, was very well received by the community, then swept the market rapidly after 1992. Yet, the Li^o electrode is still unsurpassed in energy density, not only for its intrinsic capacity, but as it can act as its own current collector, without the need for heavy and depletable copper.

From the early beginning ^[3], polymer electrolytes would show good chemical compatibility with lithium and provided that remnant crystallinity sources of current inhomogeneities are absent and the lithium interface is made with a friendly SEI. A > 1000 cycle life was recently confirmed by spectacular *in operando* observation of a functioning cell ^[4]. Indeed, there are > 5000 EVs equipped with Li^o/LFP batteries and the batteries are expected to last 10 years.

This utilization of lithium metal has been obtained with electrolytes that reach useful conductivities in the 60°- 80°C range, which limits the market to large systems. Though it is at a very early stage, a first family of polymers different from PEO have been recently shown to operate, though at low C/ rate, at room temperature ^[5].

Lithium is not the only element considered for future storage systems. Na as a electrochemical vector must certainly play a role due to the gigantic demand for load-levelling of renewable energies, and Na^o, though little information is presently known on its interface with electrolytes, is a candidate. The two other elements under consideration, Mg and Al, in contrast to the alkali metal have known electrolytes that can plate the metals in fine-grained, dendrite-free deposits, but both lack high capacity reversible positive electrodes. All these options will be discussed.

[1] B.C.H. Steele, in: Fast Ion transport in Solids, ed. W. Van Gool, North-Holland, Amsterdam, 1973 p. 103; M.B. Armand, *ibidem*, p. 665.

[2] M. S. Whittingham, *Science*, 192 (4244), 1976, pp. 1126-1127

[3] M. Armand, J.M. Chabagno, M. Duclot, Fast Ion Transport in Solids, P. Vashishta ed., North Holland New-York, 1979 p. 131.

[4] P. Hovington, M. Lagacé, A. Guerfi, P. Bouchard, A. Mauger, C. M. Julien, M. Armand, and K. Zaghib, *Nano Lett.*, 15 (4), 2015, pp 2671–2678

[5] J Mindemark, B. Sun, Erik Törmä, D. Brandell, *J. of Power Sources* 298, 2015, 166 -170