



Déclaration d'intention pour demande de bourse de thèse CEMAM

IRP principal: IRP5

IRP secondaire: IRP 2

Title: Nano-architected multifunctional composite electrodes for Li-air batteries

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Teams involved within CEMAM: LEPMI: EI, CMESSIE; SIMAP: TOP; CMTC

Industrial partner involved: HUTCHINSON, a 100% affiliate of Total (David Aymé-Perrot)

Context:

The present endeavor for electrified vehicles and small mobile electronic devices renders mandatory to develop electrochemical generators of higher energy density and greater safety than the present state-of-the-art Li-ion batteries. The latter are indeed bounded to energy-densities below 200 Wh kg^{-1} , while they are concerned by safety issues owing to the fact that both the reducer and oxidant are stored in the same system once charged. On the contrary, in Li-air batteries, the oxidant is not stored in the system, thereby corresponding to greater safety of usage and much larger energy density, at least in theory. To render this system viable, research must be devoted to the positive oxygen electrode, to favor sufficiently fast oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) in non-aqueous electrolytes. The oxygen electrode indeed exhibits multiple limitations, owing to the formation of complex discharge products, like O_2^- radical and Li_2O_2 , two species that are very aggressive to their environment, the latter being prone to crystallization onto its site of production and further passivation of the electrode surface. In consequence, the re-charge of the Li_2O_2 layer is often problematic and only partial, which conveys dramatic issues in terms of charge/discharge efficiency and system cyclability.

Rationalizing the processes taking place at the positive electrode (to obtain larger discharge currents, extended cyclability and longer durability) can be achieved (to some extent) via a strict control of the electrode morphology, where one wants to (i) emphasize the rate of O_2 mass-transport from the storage (the ambient air, or O_2 tank) to the active sites where the reaction takes place, which suggest "gas channel" exists, or that the electrolyte immobilized in the pores of the positive electrode active layer is capable of adequately leading to fast O_2 diffusion and (ii) heighten the area of interaction between the electrode/electrocatalyst material (usually carbon), the electrolyte and the reactant (O_2). Carbon structures are usually the key material of the positive electrode of a Li-air battery. Obviously, knowing the intrinsic instability of carbon towards the environment of the positive electrode of a Li-air battery, its coating with a protecting conductive (oxide or nitride) layer may be interesting.

In the present project, we will deposit oxide/nitride layers (via Atomic Layer Deposition, ALD) at flat (model) / or textured (technological) carbon surfaces to protect these carbon structures. We will then electrochemically characterize these composites in view of their oxygen reduction reaction and oxygen evolution reaction activities and durability. The mechanisms of the ORR and OER as well as the possible electrode materials / electrolyte degradations will be studied by *in situ* coupling electrochemistry and physicochemical methods (FTIR, Raman, DEMS), all available in-house at LEPMI. Then, the best materials / structures will be assembled in positive electrodes, in conjunction with a porous PTFE network to emphasize the oxygen mass-transport, and tested in Li-air cells, in partnership with HUTCHINSON.