Development and choice of catalysts for positive electrode of lithium−air batteries

Charles Gayot[a], Nicolas Guillet[a], Sophie Mailley[a], Lionel Picard[a], Gérard Gebel[b]
[a] CEA Grenoble / LITEN
[b] CEA Grenoble / INAC/SPrAM
17, rue des martyrs 38054 Grenoble Cedex 9 – France

As the need for energy storage increases, a new technology bringing higher energy density must be developed. The lithium-air battery is a good candidate among the new battery technologies to meet the challenge[1-3] having a specific energy of 1300Wh/kg with an alkaline electrolyte. The lithium−air battery with alkaline electrolyte is composed by metallic lithium, a physical protection of the lithium to avoid its contact with water, aqueous electrolyte and a reversible air electrode.

The development and the optimization of the catalysts used in the air electrode[4-6] goes through the determination of the intrinsic catalytic activity of the latter[7-9].

Here we used an electrochemical technique, namely the cyclic voltammetry (CV) using a rotating ring-disk electrode (RRDE), in order to discriminate the catalytic activity of different supported catalysts for the reaction of oxygen reduction (ORR). We studied carbons usually utilized as Ketjenblack EC-300J, EC-600JD and Timcal Super C65 in a lithium hydroxide solution at 1 mol·L^{-1} saturated in oxygen. Two catalysts (α-MnO_2 and β-MnO_2) were prepared by hydrothermal synthesis, characterized by SEM and studied as well in the same conditions. The α-MnO_2 catalyst is a nanowire with ca. 60 nm width and 3 µm length. The β-MnO_2 exhibits a spherical morphology with many nanowires on its surface.

Figure 1 shows the polarization curve for the ORR of the carbons and the catalysts above-cited deposited of glassy carbon tested in a solution of LiOH 1 mol·L^{-1}.

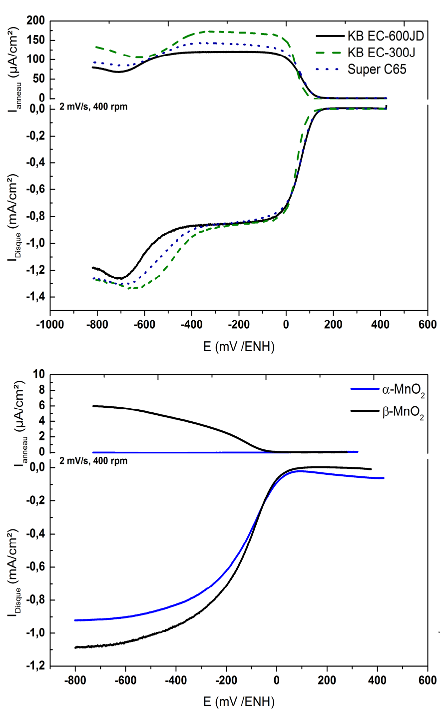

Figure 1 : (a) CV of carbones Ketjenblack EC-600JD, EC-300J and Super C65 and (b) α-MnO_2 and β-MnO_2 on RRDE at 2 mV/s, 400 trs/min between 420 mV_{ENH} et -820 mV_{ENH} in a solution of LiOH 1M saturated in O_2.

Carbons reduce oxygen with a two-steps reaction when they are used in an alkaline medium with LiOH : first in HO_2^- and then OH^- namely :

$$O_2 + H_2O + 2e^- \rightarrow OH^- + HO_2^-$$
$$HO_2^- + 2e^- + H_2O \rightarrow 3OH^-$$

Figure 2 shows the production of HO_2^- as a function of disk potential of the rotating electrode for the Ketjenblack EC-600JD and the β-MnO_2. The production of HO_2^- by the catalysts is as low as 3% for β-MnO_2 and less than 0,15% for α-MnO_2. The reaction of reduction of O_2 can be considered like "direct".

The production rate of HO_2^- is obtained with the equation here below:

$$\%\ HO_2^- = \frac{200 \times J_{anneau}}{N \times (J_{disque} + \frac{J_{anneau}}{N})}$$

With N the collection coefficient that is proportional to the generated species at the disk and transported to the ring to be collected.

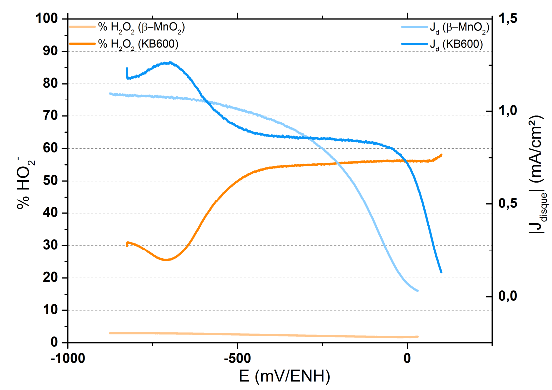

Figure 2 : Production of HO_2^- as a function of the disk potential of the rotating electrode for the carbon KB EC-600JD and the catalyst β-MnO_2.

CV with RRDE is an easy technique that can be easily used to evaluate the relative performance of different possible catalysts for the air electrodes in lithium−air batteries. The catalysts currently undergo tests for being validated in a complete cell.

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