

### Synthesis, Characterization and Electrochemical Investigation of MnO<sub>2</sub> Chemically Deposited on Carbon for Li/Air Batteries

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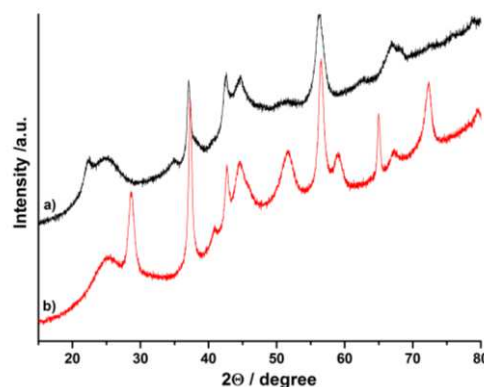
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Switching from an intercalation compound in a Li-ion battery to a catalytically active oxygen electrode is expected to result in a 4-fold higher specific energy of the positive electrode [1]. For this reason, Li/air batteries have attracted a continuously growing interest since they were introduced by Abraham et al. [2]. However, important issues such as poor rate capability, poor cycle life, and low round trip efficiency are still faced. The latter is related to the overpotentials for oxygen reduction and evolution reactions (ORR and OER) at the air cathode, for which carbon composite electrodes with different catalysts have been considered. Pt/Au catalysts supported on carbon have been reported to exhibit very good catalytic activities for ORR and OER and yield capacities > 1500 mAh/g<sub>C</sub> [3]. Nevertheless, the high costs of these precious metals hinder their application in Li/air batteries; therefore replacement of these noble metals with non-noble transition metal oxides has been the subject of research since many years.

Much attention is now being focused on MnO<sub>2</sub> phases, not only due to their remarkable activities in enhancing the voltage round trip efficiency of a Li/air cell (≈ 70% for MnO<sub>2</sub> [4] compared to ≈ 75% for Pt/Au [3]), but also because of their low costs and toxicity. Among the MnO<sub>2</sub>/C electrode preparation methods, chemical deposition of MnO<sub>2</sub> directly on the carbon surface is of particular interest; such a synthesis has the advantages of creating intimate interfaces between the oxide and the carbon which provide improved electric conductivity, nano sized oxide particles, controllable thickness [5] and highly uniform MnO<sub>2</sub> coatings on the carbon substrate. Nevertheless, the formation of different MnO<sub>2</sub> phases (α, β, ε, δ, λ) is strongly dependent on the synthetic parameters (pH of the medium, temperature, mole ratio of the precursors, etc.). Moreover, synthesis of these phases on the carbon is another challenge; because, depending on the reaction medium, carbon can easily be oxidized, and this may affect the phase of MnO<sub>2</sub> formed on the surface.

In order to understand the influence of several synthetic conditions on the morphology of MnO<sub>2</sub> chemically deposited on the carbon support, we prepared nano sized MnO<sub>2</sub>/carbon composites in different routes and studied the resultant MnO<sub>2</sub>

crystalline phases by SEM, TEM, and XRD techniques. Figure 1 illustrates the XRD patterns recorded for the two of MnO<sub>2</sub> phases obtained directly on carbon. The chemical compositions of the materials were determined by CHNS analyzer and TGA/DSC-MS. BET surface area of the samples was also calculated using nitrogen-sorption porosimetry technique.



**Figure 1.** XRD patterns of chemically deposited a) ε-MnO<sub>2</sub>, and b) β-MnO<sub>2</sub> on Vulcan XC-72

For the electrochemical characterization of the materials, cyclic and rotating (ring) disk electrode voltammetry experiments in an alkaline-aqueous environment were carried out. In addition, the activity towards Li<sub>2</sub>O<sub>2</sub> oxidation has been evaluated in a non-aqueous Li/air battery cell combined with a mass spectrometry study of the gases being evolved. Results showed significant improvements of the round trip efficiency which means that they are promising ORR and OER catalysts to be used in Li/air cathodes.

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