ABSTRACT

NanoInnovation 2018

Synergistic electro-catalysis of core/shell Pd/PdO nanoparticles and Cr(III)-doped $NiCo_2O_4$ nanofibers in aprotic Li-O_2 batteries.

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Aprotic Li-O_2 batteries (aLOBs) exploit the reversible electrochemical formation/dissolution of Li_2O_2 in non-aqueous electrolytes. This redox reaction promises outstanding theoretical performance (e.g. energy density of 3305 Wh kg^{-1}) but its implementation in secondary battery devices still faces fundamental and technological challenges for all the cell constituents (e.g. positive and negative electrodes, electrolytes, gas management system, etc.).
Focusing on the positive side, an efficient electrode for aLOBs needs to be electrically conductive, porous, able to accommodate the precipitation/dissolution of Li_2O_2 particles, easily wetted by the electrolyte and capable to electro-catalyze both the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER). Moreover it should also be chemically and electrochemically inactive in the highly oxidizing environment of an aLOB, where radicals and strong nucleophilic species can be originated upon cycling.
In this communication we illustrate the co-catalysis in aLOBs of C-free nanostructured mixed oxide electrodes decorated by Pd/PdO core/shell nanoparticles. A Cr(III) doped $NiCo_2O_4$ material has been grown hydrothermally on an open Ni-mesh. Palladium nanoparticles have been synthesized by pulsed lased ablation in liquid acetone in the fs regime, deposited by drop casting onto the surface of the nanostructured mixed oxide electrodes and the resulting electrodes have been calcined at 300°C. The use of laser techniques to produce nanoparticles for aLOBs is here proposed for the first time in the literature, as well as the peculiar combination of Pd/PdO core-shell nanoparticles deposited onto C-free Cr(III) doped $NiCo_2O_4$ self-standing electrodes. Performance in aprotic Li-O_2 batteries have been recorded in galvanostatic conditions and post mortem analysis of the electrode surfaces have been carried out by X-ray photoemission spectroscopy. The use of core/shell Pd/PdO nanoparticles as co-catalysts enhances the reversibility of the electrochemical oxygen reduction/evolution reactions. This beneficial effect originates by the decrease of the mean overvoltages compared to the bare Cr(III) doped $NiCo_2O_4$ electrodes and extends the cell calendar life of the electrochemical device.