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Featured Letter

Enhancement of the performance in Li-O_2 cells of a $NiCo_2O_4$ based porous positive electrode by Cr(III) doping

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ABSTRACT

Here we discuss the incorporation of Cr(III) as dopant in the spinel lattice of the $NiCo_2O_4$ cubic phase and its beneficial effect on the electro-catalytic activity of this material in aprotic Li-O_2 cells. To this aim, we synthesized highly porous carbon-free self-standing electrodes constituted by nanostructured undoped and Cr-doped $NiCo_2O_4$ grown on open nickel mesh. These materials were characterized by X-ray diffraction, field emission scanning electron microscopy coupled with energy dispersive spectroscopy, transmission electron microscopy and X-ray photoelectron spectroscopy. The performance in aprotic Li-O_2 cells of the undoped and Cr-doped $NiCo_2O_4$ electrodes were tested in galvanostatic cycling using a LiTFSI 1 m in tetraethylene glycol dimethyl ether electrolyte without the incorporation of any carbon conductive agent. Cr(III) doping discloses a remarkable enhancement of more than 300% of the discharge capacity at $J = 0.1\ mA\ cm^{-2}$. Moreover, the Cr-doped $NiCo_2O_4$ material is capable to give reversible limited capacity ORR/OER for 52 and 45 cycles at $0.2\ mA\ cm^{-2}/0.1\ mAh\ cm^{-2}$ and $0.1\ mA\ cm^{-2}/0.2\ mAh\ cm^{-2}$, respectively, without oxygen flow in static Ar/O_2 overpressures ($p_{O2} = 1 bar$). Pseudo-Tafel data derived by galvanostatic titrations highlight the beneficial effect of Cr(III) doping on the electrode kinetics both for ORR and OER.

1. Introduction

Aprotic Li-O_2 electrochemical cells are an emerging technology able to supply very high energy densities [1], thus making possible their use for the electric transportation [2]. However, the state-of-the-art performance is not aligned to the theoretical one due to various challenging open issues widely studied worldwide [3,4]. One may easily recall the limited chemical stability of the lithium metal negative electrode upon cycling [5] and the complex instabilities of both the non-aqueous electrolytes [6] and the carbon positive electrodes [7] during cell discharge and charge, thus leading to the accumulation of insoluble reaction byproducts within the pore of the positive electrode and to the cell death [1].

An aprotic Li-O_2 cell exploits the reversible electrochemical precipitation/dissolution of Li_2O_2 within the porous structure of the positive electrode. The Li_2O_2 crystal growth during the cell discharge (ORR, oxygen reduction reaction) takes place by a complex mechanism [3] that can occur both in solution and on the electrode surface depending on the nature of the electrolyte components [8]. Moreover, the nature/morphology of the positive carbon-based electrode, that acts as an electro-catalyst, also plays a major role in the facilitation of the growth of Li_2O_2 crystallites vs. amorphous films [9].

Going beyond the carbon electro-catalysts, mixed transition metal oxides are known as good electro-catalysts for both the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER) [10]. Particularly, cubic mixed transition metal oxides, like $NiCo_2O_4$ or $CoMn_2O_4$, are able to give good catalytic activity in aprotic Li-O_2 cells [11–15]. As already mentioned, the use of carbon-free electro-catalysts prevents its degradation upon cycling due to the complex parasitic reactivity involving both solvent and carbonaceous components of the electrodes [6,7].

In this work, we discuss the incorporation of Cr(III) as dopant in the inverse spinel lattice of the $NiCo_2O_4$ cubic phase and the beneficial effect on the catalytic activity of this material in aprotic Li-O_2 cells. To this aim, we synthesized highly porous monolithic electrodes constituted by nanostructured $NiCo_2O_4$, undoped and Cr(III)-doped, grown on open nickel mesh by a hydrothermal route. Both materials were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) coupled with energy disper-

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sive spectroscopy (EDS), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). The performance in Li-O_2 cells of both $NiCo_2O_4$ materials were tested in galvanostatic cycling using a LiTFSI 1 m in tetraethylene glycol dimethyl ether electrolyte.

2. Experimental method

Cr(III)-doped $NiCo_2O_4$ (NCCr@Ni) and undoped $NiCo_2O_4$ (NC@Ni) materials were grown on a nickel mesh by means of a hydrothermal method according to the literature [13], with minor modifications to incorporate $Cr(NO_3)_3{\cdot}9H_2O$ in the precursors solution. The Ni foam was punched into discs with a diameter of 14 mm, degreased with acetone, etched with HCl 6 M for 10 min, rinsed with deionized water and absolute ethanol and then dried at 333 K. Weighted amounts of the cobaltite precursors (0.474 g $CoCl_2{\cdot}6H_2O$, 0.237 g $NiCl_2{\cdot}6H_2O$, 0.18 g urea and in the case of the doped material 0.08 g $Cr(NO_3)_3{\cdot}9H_2O$, Cr(III) molar concentration was 1/10 compared to that of cobalt) were dissolved in 30 mL H_2O. The resulting solution was transferred into a 50 mL Teflon lined stainless autoclave together with 8 pre-treated Ni foam discs, sealed and kept at 120 °C for 6 h. The obtained composite disks were washed with water, dried at 60 °C for 10 min and finally calcined at 300 °C for 4 h in air. Approximately, the cobaltite loading on each disk was ~1 mg cm^{-2}. The XRD experiments have been carried out using a Rigaku X-ray Ultima + diffractometer equipped with a CuKα source and a graphite monochromator for the diffracted beam. The cubic cell parameter has been derived by the well-known Bragg equations and the crystallite size by the Scherrer equation. We deliberately avoided a full Rietveld refinement due to the presence of massive metallic nickel diffraction peaks partially superimposed over the reflections of the other nanostructured components of the electrodes. Surface area measurements have been obtained by single point N_2 absorption using a Monosorb Quantachrome instrument. XPS spectra were recorded using a modified Omicron NanoTechnology MXPS system equipped with a monochromatic X-ray source (Omicron XM-1000) and an Omicron EA-127 energy analyzer. The exciting radiation was Al Kα ($h\upsilon$ = 1486.7 eV), generated operating the anode at 14–15 kV and 10–20 mA. More technical details can be found elsewhere [7]. The C 1s binding energy (BE) of the –CH_2– groups at 284.8 eV belonging to the aliphatic carbon contamination on the cathodes surface was used as an internal standard reference for the BE scale (accuracy of ±0.05 eV). FE-SEM experiments were recorded by a Zeiss Auriga electron microscope equipped with a field emission source and a Bruker energy dispersive X-ray spectroscopy (EDS) probe. TEM observations were recorded using a FEI Tecnai 200 kV cryo-TEM instrument. Fast-fourier transform analyses of the TEM micrographs have been carried out using the ImageJ software to derive the simulated electron diffraction pattern [16]. Li-O_2 electrochemical cells preparation was realized in a Iteco Engineering argon-filled glovebox using ECC-AIR cells by EL-CELL: a metallic lithium coin has been coupled with a glass-fiber separator (Whatman) impregnated with 150 μL cm^{-2} of a non-aqueous electrolyte and the positive electrode. The electrolyte was a 1 molal solution of LiTFSI dissolved in TEGDME (Sigma-Aldrich, moisture controlled grade). The ~3 cm^3 dead-volume above the positive electrode was filled with an overpressure of O_2 (5.0 purity). The final starting oxygen partial pressure was 1.0 bar. Electrochemical tests were carried out by using a MTI Corp. battery cycler: currents regimes were set in terms of current densities (J) by dividing for the geometrical area of the cathodes (1.54 cm^2). A pseudo-Tafel plot has been derived from intermitted galvanostatic titrations experiments performed at various current densities. Electrodes have been partially pre-discharged with a voltage cut-off fixed at 2.6 V vs. Li at 0.025 mA cm^{-2} and then, after 12 h of relaxation in open circuit conditions (OCV), a constant current density signal (J) has been applied followed by 6 h of cell relaxation in OCV. Nine J values have been sampled both in ORR and OER (±1.3, ±3.3, ±6.5, ±13, ±32.5, ±65, ±130, ±325, ±650 μA cm^{-2}, respectively) by partially discharging/charging the electrodes with a capacity limitation of ±0.01 mAh cm^{-2}, in order to restore after each polarization the starting electrode composition.

3. Results and discussion

The results of the physico-chemical characterization of the two undoped and Cr-doped materials, i.e. NC@Ni and NCCr@Ni, respectively, are shown in Fig. 1.

Both for NC@Ni and NCCr@Ni the diffraction patterns (Fig. 1a) show the characteristic peaks of a cubic $NiCo_2O_4$ phase crystallized in an inverse spinel lattice (space group Fd$\bar{3}$m 227, JCPDS Card No. 73-1702) where Ni occupies the octahedral 16d sites and Co is distributed in both the 16d and the tetrahedral 8a sites [17]. Further XRD peaks can be attributed to the Ni mesh (space group Fm$\bar{3}$m 225, JCPDS Card No. 04–0850) and traces of NiO (space group Fm$\bar{3}$m 225, JCPDS Card No. 73-1523) possibly grown from the Ni mesh due to its spontaneous corrosion in alkaline aqueous solutions [18]. The cell parameter of the NCCr@Ni material is larger (i.e. a = 8.128 ± 0.003 Å) compared to the undoped NC@Ni (i.e. a = 8.117 ± 0.005 Å, in line with ref. [19]). Considering that most studies suggest that both Ni and Co can have mixed (II) and (III) oxidation states in the lattice [17], the cell expansion in the NCCr@Ni material matches well with the substitution in the lattice of Ni(II)/Ni(III) and Co(II)/Co(III) ions with the larger Cr(III) ions (Shannon ionic radii 0.550, 0.560, 0.580, 0.545 and 0.615 Å for Ni(II), Ni(III), Co(II), Co(III) and Cr(III), respectively) [20]. The crystallite sizes estimated from the XRD patterns are 23 ± 4 and 17 ± 4 nm for the NC@Ni and NCCr@Ni materials, respectively.

From the morphological point of view, both NC@Ni and NCCr@Ni are constituted by porous nanowires of approximately 50–150 nm in diameter and 1–3 μm in length (see the FE-SEM images in Fig. 1b and e). TEM analyses (see Fig. 1c and f) suggest that these nanowires are formed in both cases by highly crystalline regular particles (see the simulated electron diffraction patterns for both NC@Ni and NCCr@Ni in Fig. 1c and f) with linear size in the 20–30 nm range [17], in reasonable agreement with the XRD. This morphological similarity is also confirmed by the values of the surface area that are 37 and 42 $m^2\,g^{-1}$ for the NC@Ni and NCCr@Ni, respectively. The EDS analyses suggest Ni/Co ratios of 0.62 ± 0.18 and 0.68 ± 0.17 for NC@Ni and NCCr@Ni, respectively, in reasonable agreement with the 0.5 bulk stoichiometry, and considering the possible influence of the underlying Ni mesh. The experimental Cr/Co ratio in the NCCr@Ni material is 0.2 ± 0.2, slightly exceeding the expected 0.1 value. The EDS map of chromium (Fig. 1d) shows its homogeneous dispersion on the nanomorphologies thus confirming its incorporation as dopant into the spinel lattice.

The Ni $2p_{3/2}$, Co $2p_{3/2}$ and Cr 2p XPS spectra of the two NC@Ni and NCCr@Ni materials are shown in Fig. 2. The profile of the Ni $2p_{3/2}$ signal in the undoped NC@Ni sample (Fig. 2a, lower spectrum) is fully compatible with already reported data on the same compound [21–23], while a decrease in the intensity of the shoulder at ~856 eV can clearly be seen for the Cr(III)-doped material (Fig. 2a, upper spectrum). In NiO this shoulder has been widely accepted to be due to non-local screening effects in the final ionized states of Ni(II) sites [24] whereas, in spinel phases, its attribution to Ni(III) centers has been proposed by many authors [22,25,26]. Thus, our experimental evidence suggests that the dop-