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Oxygen evolution reaction at the surface of nickel cobaltites: The impact of surface restructuring phenomena on the activity

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The storage of intermittent renewable energies requires the implementation of efficient energy storage systems. These systems must allow converting renewable energies into sustainable energetic vectors (hydrogen, electron). For this purpose, the oxygen evolution reaction (OER) plays an important role. OER possesses a sluggish kinetics that can be enhanced by using a catalyst exhibiting reliable surface composition and morphostructural properties. To limit the use of scarce noble metals, the synthesis of effective 3D transition metal oxide-based catalysts is of interest. As activity and stability of materials depend on their composition and morphostructural properties, the synthesis of well-defined catalysts is of utmost importance. To this end nanocasting approach constitutes an interesting pathway. In this study, $NixCo_3$-xO_4 materials have been synthesized by replicating ordered mesoporous silica templates. Materials were investigated using numerous physico-chemical techniques such as x-ray induced photoelectron spectroscopy (XPS), high resolution transmission electron microscopy, x-ray diffraction and Raman spectroscopy. Evidences from XPS and Raman measurements reveal that the different catalysts surfaces are hydroxylated. A particular attention was paid to restructuring phenomena occurring upon potential cycling and responsible for greatly improving the OER activity. These restructuring phenomena were evidenced using post-mortem Raman spectroscopy and XPS. It was observed that the intrinsic activity of the different restructured catalysts depends on the incorporated nickel amount and correlates with the CoIII/CoIV peak potential. The modulation of CoIII/CoIV peak potential is explained by changes in the chemical environment of surface Co atoms and results in the formation of nickel/cobalt oxy-hydroxide. Nickel indeed modulates the electronic properties of the Co active site and allows improving the OER activity of electrode materials. The catalysts described in this presentation are moreover very efficient since after surface restructuring, the overpotential at 10 mA.cm^{-2} is as low as 310 mV.

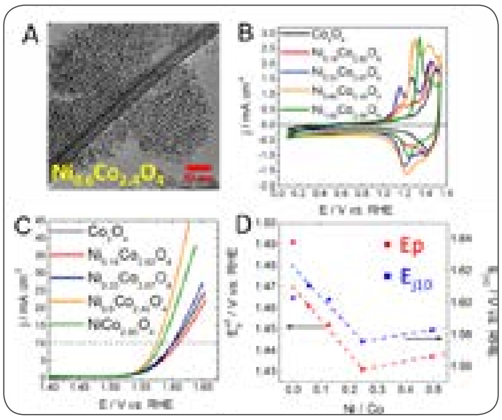

Figure 1: A) TEM image of $Ni_{0.6}Co_{2.4}O_4$ catalyst. **B)** Cyclic voltammograms of $Ni_xCo_yO_4$ recorded in a 1 mol L^{-1} KOH electrolyte. Scan rate 20 mV s^{-1}
C) OER polarization curves recorded with $Ni_xCo_yO_4$ in a 1 mol L^{-1} KOH electrolyte. Scan rate 5 mV s^{-1}

D) Correlation between position of CO_3+/CO_4+ redox transition (red dots) and OER overpotential at 10 mA cm^{-2} (blue dots)

Recent Publications

1. Abidat I, Bouchenafa Saib N, Habrioux A, Comminges C, Canaff C, Rousseau J, Napporn T, Dambournet D, Borkiewicz O and Kokoh K (2015) Electrochemically induced surface modifications of mesoporous spinels (Co_3O_4-δ, $MnCo_2O_4$-δ, $NiCo_2O_4$-δ) as the origin of the OER activity and stability in alkaline medium. Journal of Materials Chemistry A 3:17433-17444.
2. Abidat I, Morais C, Comminges C, Canaff C, Rousseau J, Guignard N, Napporn T W, Habrioux A and Kokoh K B (2017) Three dimensionally ordered mesoporous hydroxylated $NixCo_3$-xO_4 spinels for oxygen evolution reaction: on the hydroxyl-induced surface restructuring effect. Journal of Materials Chemistry A 5:7173-7183.
3. Kumar K, Canaff C, Rousseau J, Arrii Clacens S, Napporn T W, Habrioux A and Kokoh K B (2016) Effect of the oxide-carbon heterointerface on the activity of Co_3O_4/NRGO nanocomposites toward ORR and OER. Journal of Physical Chemistry C 120:7949-7958.
4. Kumar K, Loupias L, Canaff C, Morisset S, Pronier S, Morais C, Habrioux A, Napporn T W and Kokoh K B (2018) Preparation and electrochemical properties of $NiCo_2O_4$ nanospinels supported on graphene derivatives as earth-abundant oxygen bifunctional catalysts. ChemPhysChem 19:319-326.
5. Kumar K, Abidat I, Canaff C, Morisset S, Habrioux A, Morais C, Napporn T W and Kokoh K B (2018) Metal loading effect on the activity of Co_3O_4/N-Doped reduced graphene oxide nanocomposites as bifunctional oxygen reduction/evolution catalysts. ChemElectroChem 5:483-493.

Biography

Aurélien Habrioux (Associate Professor) has an expertise in electrocatalysis and in materials science. His research interests deal with the design and development of novel non-noble electrocatalysts for reactions such as oxygen reduction reaction and oxygen evolution reaction in alkaline medium. He is especially interested in scrutinizing and explaining surface restructuring phenomena affecting catalysts surface and occurring upon working conditions. He has been coordinating researches aiming at developing transition metal oxides supported heteroatom doped graphene-based materials for the reversible air electrode of high energy density Li-air and Zn-air batteries. He has also been working on the understanding of the effect of the active phase/substrate interaction on the electrocatalytic activity.

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