## Study of the effect of the Pt shell coverage on Ni core for the oxygen reduction reaction

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The most important issue that needs to be addressed in promoting the widespread use of fuel cell devices is cost reduction. Especially, it is of vital importance to reduce platinum loading of catalyst layers (CL). One strategy for reducing cost is to decrease the amount of Pt loading i.e., using Pt more effectively [1]. In fact, according to New Energy and Industrial Technology Development Organization (NEDO), the target of Pt loading is to use less than 0.1 g/kW [2]. In order to accomplish such a reduction of Pt loading in fuel cells, it is necessary to critically assess the use of Pt contained in the CL of the membrane electrode assembly (MEA). Thus the development of new Pt-based catalysts, with superior electrocatalytic activity and improved active surface area utilization is very important. In terms of the catalytic activity, core-shell catalysts have been recently under intense investigation [3-5]. The Pt mass activity of these Pt monolayer electrocatalysts for the oxygen reduction reaction (ORR) can be several times higher than that of commercial Pt/C materials [6]. In this work, the catalyst preparation, structural and electrochemical characterization is used as a basis for the determination of the intrinsic properties of Ni@Pt core-shell electrocatalyst for the ORR in acid media with a series of different Pt loading coverage's on a nickel core.

Fig. 1 presents the narrow scans of Ni2p and Ni3p-Pt4f core-level of XPS for Ni@Pt catalysts with different Pt loadings (0-30 w/w %). The spectra show a fairly homogeneous core distribution for all catalysts. On the other hand the Pt4f core-level response increases with increasing Pt loading.
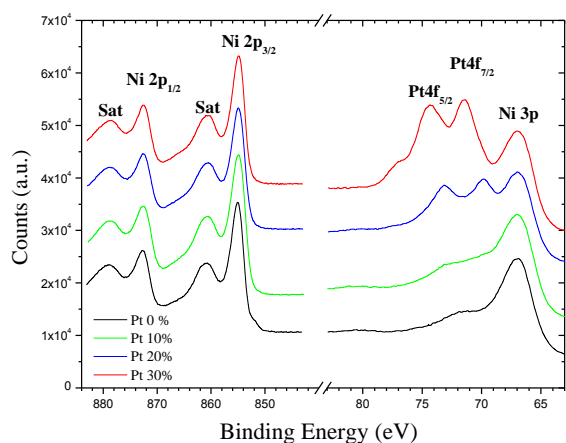


Fig. 1. XPS spectra of Ni2p and Ni2p-sat and 3p-Pt4f electronic core level for different Ni@Pt core-shell catalysts with different Pt loading coverages.

Detailed observation of the Ni@Pt naoparticles (Pt 20 wt%) has been performed by atomic resolution electron microscopy. The core-shell morphology can be discerned for coverage of two Pt layers on Ni, however some missing Pt atoms were also detected (Fig. 2a). The core

and shell can be identified on the basis of their scattered intensities measured directly on the atomic columns image (Fig. 2b). Differences in the bond distances between internal and outer atoms reflected a strain feature caused by lattice parameter mismatch between Pt and Ni.
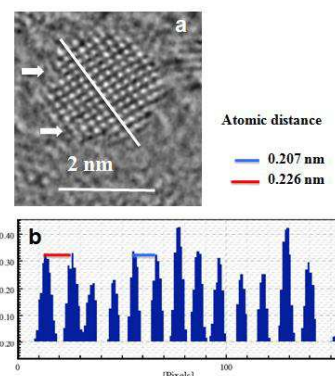


Fig. 2. a) HRTEM imagen of the Ni@Pt (Pt 20 wt %). b) Phase of scattered intensities.

Preliminary electrochemical results for the oxygen reduction reaction (ORR), have shown that the kinetic properties are intrinsically related to the amount of Pt on Ni. The Fig. 3 shows specific activity $J_k$ and mass activity $J_m$, obtained after mass transport correction at 0.8 V. Both specific and mass activities increase with decreasing Pt loading on Ni. This behavior can be related with a Pt structural strain promoted by Ni coordination in the interface, which would be less pronounced as the number of Pt layer grows. However more detailed studies are mandatory.
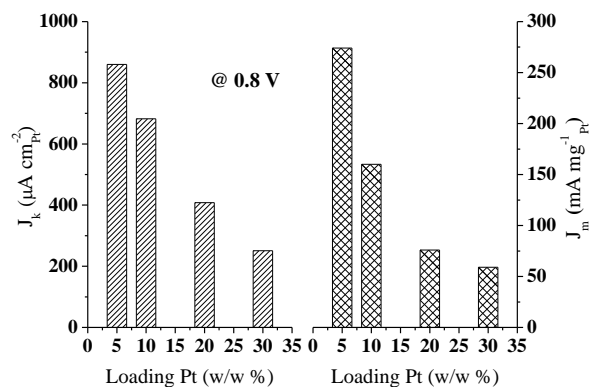


Fig. 3. Specific activity (Jk) and mass activity (Jm) versus Pt shell-loading on Ni after mass transport correction at 0.8 V. The data were obtained from steady state polarization curves for the ORR (after capacitive current correction) in $O_2$ saturated 0.5 M $H_2SO_4$ at 20 mV s$^{-1}$ and 1600 rpm.

References: [1] H.L. Gao et al. J. Pow.Sources; 195 (2010) 756-761. [2] New Energy and Industrial Technology Development Organization (NEDO) http://www.nedo.go.jp/nenryo. [3] A. Manthiram et al. Langmuir; 28 (2012) 1579-1587. [4] R.R. Adzic et al. Electrochim. Acta; 55 (2010) 2645-2652. [5] O. Solorza-Feria et al. Int. J. Hydro. Energ. 37 (2012) 14902-14910. [6] R.R. Adzic et al. 109 (2005) 22701-22704.

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