

# Electrochemical Valorization of Glycerol on Ni-rich Bimetallic Nanoparticles: Insight into Activity and Product Selectivity

Mohamed S.E Houache

Department of Chemical and Biological Engineering, Centre for Catalysis Research and Innovation, University of Ottawa, 161 Louis-Pasteur Ottawa ON, Canada, K1N 6N5

Glycerol partial electrooxidation to produce various chemicals has attracted a great amount of attention in the last years [1]. Glycerol is the main by-product of biodiesel production from vegetable oils and animal and/or waste fats and for each 10L of biodiesel one litter of glycerol is produced. As biodiesel production increases, the overproduction of glycerol becomes problematic. Glycerol electrooxidation reaction (GEOR) without C-C bond cleavage leads to the formation of a large number of high value-added chemicals. The control of catalyst selectivity and activity could be achieved through formulation of novel, nanostructured electrocatalysts. Nickel is an attractive material for glycerol electrooxidation in alkaline media [2], due to its natural abundance and good stability in alkaline media. Designing nanostructured 3D Ni electrodes could enhance the catalytic activity of Ni, whereas its selectivity could be altered by addition of small amounts of the second metal [1].

In the present work, glycerol electrooxidation reaction (GOR) was investigated on Ni-based mono and bimetallic  $\text{Ni}_x\text{Pd}_{1-x}$  ( $x = 95, 90, 80$ ) and  $\text{Ni}_x\text{Bi}_{1-x}$  ( $x = 98, 95$  and  $90$  at. %) nanoparticles in 1M KOH. Ni nanoparticles were synthesized using polyol method in the presence of hydrazine. Variation of NaOH concentration during the synthesis resulted in formation of the shape-controlled triangular and urchin-like Ni NPs. Triangular Ni NPs were synthesized at lower concentrations (1M NaOH), while Ni urchins were fabricated at higher NaOH concentration (0.5M NaOH). Resulting Ni-based NPs were characterized using XRD, SEM, TEM, EDS mapping and HAADF imaging. Electrochemical measurements were carried out on Ni-based NPs using cyclic voltammetry (CV), chronoamperometry (CA) and linear sweep voltammetry (LSV) at room temperature. Results showed that Ni, NiPd and NiBi NPs are active for GEOR and that reaction proceeds through the formation of NiOOH active phase similar to bulk Ni electrodes [2]. Chronoamperometry coupled with *in-situ* polarization modulation infrared-reflection absorption spectroscopy (PM-IRRAS) for the simultaneous analysis of products on the Ni surface and in the bulk electrolyte solution demonstrated that the main reaction products on Ni surface are glyceraldehyde, carbonyl, carboxylate ions and some carbon dioxide. Addition of small quantities of Bi (2 and 5 at. %) to Ni significantly altered the product selectivity of GEOR facilitating tartaric acid production, which is attributed to C=O stretching of C-COO<sup>-</sup> at  $1718\text{ cm}^{-1}$ . Whereas, the carbon supported Ni-based catalysts are selective towards formate as illustrated on HPLC and NMR data.

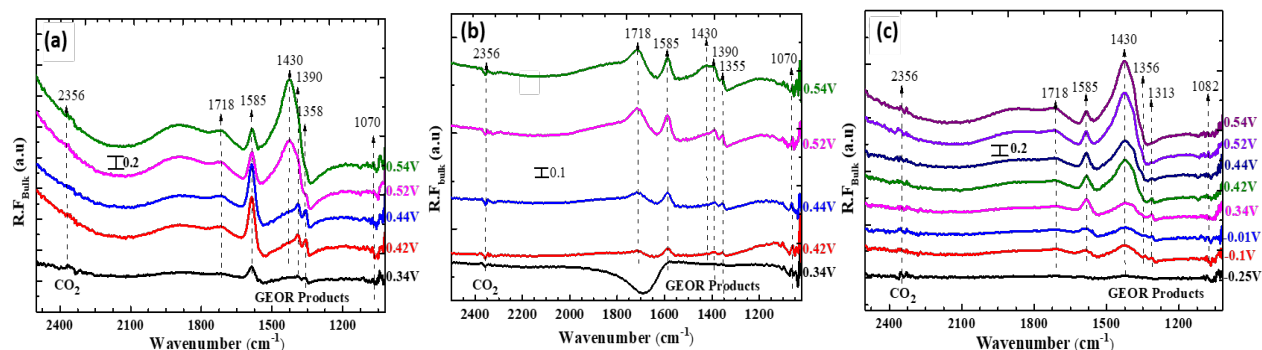


Fig. 1. PM-IRRAS spectra of GEOR products on (a) Ni, (b)  $\text{Ni}_{95}\text{Bi}_5$  and (c)  $\text{Ni}_{80}\text{Pd}_{20}$  in the thin cavity/bulk solution

## References

- [1] M. Simoes, S. Baranton, C. Coutanceau, *ChemSusChem* 5 (2012) 2106.
- [2] M.S.E. Houache, E. Cossar, S. Ntais, E.A. Baranova, J. Power Sources 375 (2018) 310.