HIGHLY EFFICIENTY PALLADIUM-BASED ANODE ELECTROCATALYTS FOR DIRECT ETHYLENE GLYCOL AND GLYCEROL FUEL CELLS

F. Vizza[1], M. Bellini[1], M. Bevilacqua, J. Filippi[1], M. Innocenti[1,2], A. Lavacchi[1], A. Marchionni[1], H. Miller[1], W. Oberhauser[1], L. Wang[1,3]

[1]Istituto di Chimica dei Composti Organometallici, Consiglio Nazionale delle Ricerche, via Madonna del Piano 10, 50019 Sesto Fiorentino (Italy) (ICCOM-CNR) ,
[2]Dipartimento di Chimica, Università di Firenze, via della Lastruccia 3, 50019, Sesto Fiorentino (FI), Italy
[3]CENMAT, University of Trieste via L. Giorgeri 1, 34127 Trieste (Italy)

Introduction

The selective conversion/production of chemicals from renewable resources with simultaneous production of energy is perhaps one of the most desirable targets in sustainable chemistry. The realization of such processes will provide energy with no overall CO_2 emissions and at the same time lead to the production of industrially relevant feedstocks. Indeed, starting from renewable alcohols, a large variety of products such as aldehydes, ketones, and carboxylic acids might be obtained. Recent results have shown that direct fuel cells can be effectively employed to convert alcohols into various oxygenates, providing at the same time good power densities, exploiting the ability of certain anode electrocatalysts to bring about the partial oxidation of the anolyte with high selectivity and fast kinetics.

Results and Discussion

Here, we describe the cogeneration of electrical energy and higher-value chemicals from the electrooxidation of ethylene glycol (EG) and glycerol (G) in alkaline media, in passive as well as active direct ethylene glycol fuel cells (DEGFCs), and in direct glycerol fuel cells (DGFCs) containing Pd-(Ni-Zn)/C as an anode electrocatalyst, that is, Pd nanoparticles supported on a Ni–Zn phase.[1] For comparison, an anode electrocatalyst containing Pd nanoparticles (Pd/C) has been also investigated. The oxidation of EG and G has primarily been investigated in half cells. The results obtained have highlighted the excellent electrocatalytic activity of Pd-(Ni-Zn)/C in terms of peak current density, which is as high as 3300 A $g_{(Pd)}^{-1}$ for EG and 2150 A $g_{(Pd)}^{-1}$ for G. Membrane-electrode assemblies (MEA) have been fabricated using Pd-(Ni-Zn)/C anodes, proprietary Fe-Co/C cathodes, and Tokuyama A-201 anion-exchange membranes. The MEA performance has been evaluated in either passive or active cells fed with aqueous solutions of 5 wt% EG and 5 wt% G. In view of the peak-power densities obtained in the temperature range from 20 to 80 °C, at Pd loadings as low as 1 $mgcm^{-2}$ at the anode, these results show that Pd-(Ni-Zn)/C can be classified amongst the best performing electrocatalysts ever reported for EG (Figure 1) and G oxidation (Figure 2). IC and $^{13}C\{^1H\}$ NMR spectroscopy have been employed to analyze the anode exhausts of galvanostatic experiments. Pd/C is a less active but more selective electrocatalyst than Pd-(Ni- Zn)/C towards the EG oxidation, yielding 89.5% of glycolate. A mixture of glycolate (>50%), oxalate (37.6 %), and carbonate (7%) was obtained with Pd-(Ni-Zn)/C. A much wider product distribution, including glycolate, glycerate, tartronate, oxalate, formate, and carbonate, was detected from the oxidation of glycerol with both Pd/C and Pd-(Ni-Zn)/C. No trace of the secondary alcohol oxidation products of G such as dihydroxyacetone, hydroxypiruvate, or mesoxalate was observed.

The remarkable electrocatalytic activity of Pd-(Ni-Zn) (Figure 3) can be associated both with the high dispersion of the metal particles and to the intrinsic properties of the Ni–Zn phase that should increase the amount of OH_{ads} groups on the catalyst surface, which are required for the formation of carboxylic acids.

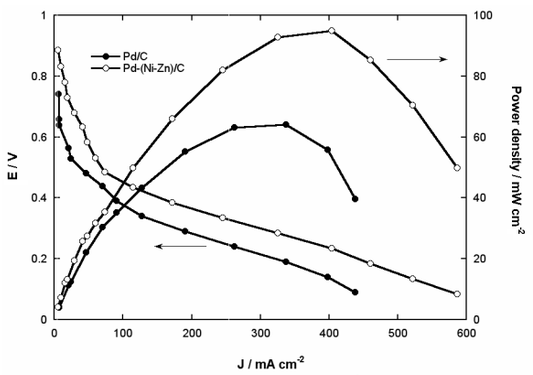

Figure 1. Potentiodynamic (scan rate 5 mVs^{-1}) and power density curves for active DEGFCs containing the Pd-(Ni-Zn)/C and Pd/C anode electrocatalysts fuelled with a 2M KOH and 5 wt% EG at 80 °C

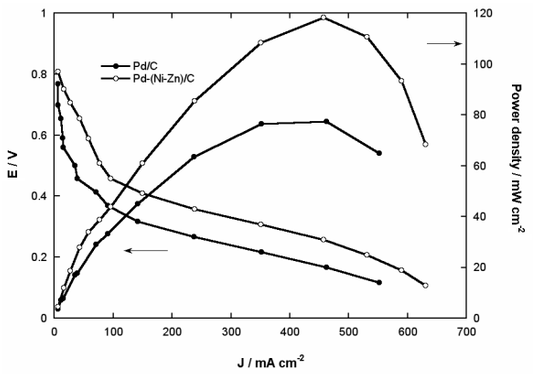

Figure 2. Potentiodynamic (scan rate 5 mVs-1) and power density curves for active DGFCs containing the Pd-(Ni-Zn)/C and Pd/C anode electrocatalysts fuelled with a solution of 2M KOH and 5 wt% G at 80 °C.

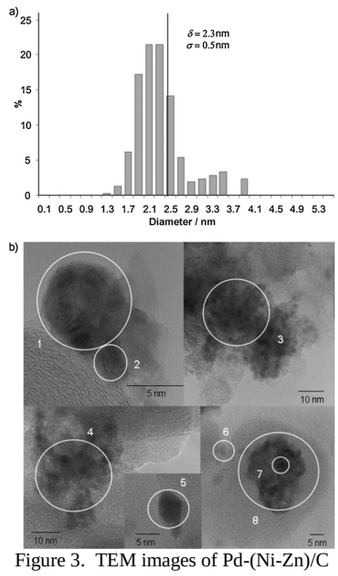

Figure 3. TEM images of Pd-(Ni-Zn)/C

[1] F. Vizza et al., ChemSusChem 6 (2013) 391-399