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Oxygen reduction reaction increased tolerance and fuel cell performance of Pt and Ru_xSe_y onto oxide–carbon composites

Laure Timperman, Aldo S. Gago, Nicolas Alonso-Vante *

Laboratory of Electrocatalysis, UMR-CNRS 6503, University of Poitiers, 40 Av. Recteur Pineau, F-86022 Poitiers, France

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ABSTRACT

Pt and Ru_xSe_y nanoparticles were selectively deposited onto oxide sites of oxide–carbon composite substrates using the photo-deposition process and compared to conventional carbon support materials. The oxide was essentially anatase phase. Cyclic voltammetry and rotating disk electrode measurements for the oxygen reduction reaction (ORR) in formic acid containing-electrolyte showed a tolerance improvement for ORR of Pt supported on composite substrates. This positive substrate effect on platinum, turned out not to be favorable for Ru_xSe_y catalyst centers. On the other hand, the methanol tolerance for ORR was increased for both nanostructured materials supported on the oxide–carbon composite. Single H_2/O_2 fuel cell results were in agreement with half-cell electrochemical measurements on Pt, showing an improvement of the power density when using the oxide–carbon as substrate for the cathode. The composites were evaluated as cathode catalysts of an HCOOH laminar-flow fuel cell (LFFC) in which commercial Pd/C was used as an anode catalyst. The cathodes with Ru_xSe_y and Pt supported on TiO_2/C improved the specific power density by 15% and 24%, respectively, with respect to carbon as support.

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1. Introduction

Nanoparticulate catalysts are supported on substrates of various natures for their use in catalysis, as well as electrocatalysis. Of particular interest is the development or modification of the most popular one: carbon (e.g., Vulcan XC-72) for technical anode or cathode electrodes for low temperature fuel cells. Chemical modification of carbon nanotubes [1–3] or nanostructured carbon [4–12] has been undertaken. Another strategy to stabilize the support is to develop metal–oxide substrates as reported for SiO_2 [13], NbO_2 [14], MnO_x [15], WO_x [16,17], SnO_2 [18] and TiO_x [15,19–28]. Pt deposited on such substrates shows an increase of the activity for the oxygen reduction reaction (ORR) as compared to Pt/C. These substrates also exhibit an enhancement of stability [22,24], and an improvement of tolerance towards carbon monoxide [17,18,29,30] and methanol [20,28,29,31–33]. Recently, it has been reported that Pd nanoparticles supported on carbon-modified TiO_2 (rutile) showed a higher activity for formic acid electrooxidation than Pd/C [34]. In this sense, fuel cell performances were also improved according to the increase of tolerance and activity for ORR.

On the other hand, micro-direct methanol fuel cells (μDMFCs) are the most attractive alternative to replace polymer lithium-ion batteries for powering portable electronics (e.g., laptops, cell phones, smart-phones, and tablet computers) [35,36]. However, their commercialization is still hindered by a number of basic problems such as methanol-crossover [37]. To overcome this issue, novel membranes with less methanol permeability or the modification of existing ones are being developed [38,39]. Nevertheless, no significant improvement on the development of alternative electrolyte membranes has been obtained so far. Laminar-flow fuel cells (LFFC), also called microfluidic fuel cells, are one alternative to μDMFCs for powering portable devices [40]. These fuel cells relay on the use of micro-channels to carry the fuel and the electrolyte-oxidant separately and thus without mixing. However, as the hydraulic diameter of the channels is reduced and its length is enlarged, fuel cross-over negative effects are evident [41]. Consequently the performance of this kind of cells is also diminished. Ru_xSe_y has been tested as cathode catalyst in DMFC, LFFC [42] and mixed reactant fuel cells [43]. Such chalcogenide catalyst has a comparable activity to Pt catalyst and a good performance for the ORR even at high concentrations of fuel. Ru_xSe_y particles were also deposited onto metal–oxide substrates and showed an enhancement of the ORR activity [16,25]. Other catalyst materials such as transition metal chalcogenides: Pt_xS_y and Co_xSe_y demonstrated to be methanol tolerant [44–46] and selective to the oxygen reduction reaction (ORR).

This work focuses on the activity for ORR and the tolerance, towards organic molecules such as formic acid and methanol, of Pt and Ru_xSe_y deposited onto oxide–carbon substrate by photo-deposition. The performance of each catalyst is further proved

* Corresponding author. Tel.: +33 54945 3625; fax: +33 54945 3580.
E-mail address: Nicolas.Alonso.Vante@univ-poitiers.fr (N. Alonso-Vante).

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