MESOPOROUS PtRu ON FIBRE-BED SUPPORTS: HIGH-PERFORMANCE ANODES FOR DIRECT LIQUID FUEL CELLS

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Introduction

The synthesis and rational design of nanostructured catalysts with characteristic dimensions such as particle size or pore diameter between 2 and 100 nm, it is of great interest for a variety of applications, including fuel cells. Direct liquid fuel cells are attractive alternatives to hydrogen, due to the higher thermodynamic energy densities of fuels such as methanol (4.4 kWh l^{-1}, DMFC) and formic acid (2.1 kWh l^{-1}, DFAFC) coupled with a simpler fuel storage and delivery infrastructure [1]. However, the sluggish CH_3OH and HCOOH electro-oxidation kinetics and the significant catalytic activity loss over time (e.g. the CH_3OH oxidation rate on Pt decreases by a factor of four to five during the first 100 ms of reaction [2]) are major challenges, imposing the use of high load of Pt-alloy catalysts. DMFCs equipped with Nafion® membranes typically require 4 mg cm^{-2} PtRu anode catalyst to achieve a peak power density of about 50 mW cm^{-2} at 333 K [3, 4]. The goal of the present work was to address the electrocatalysis challenges of the direct liquid fuel cells by investigating the synthesis and catalytic activity of PtRu nanostructures supported on graphite felt, reticulated vitreous carbon and titanium mesh creating novel extended (or three-dimensional) reaction zone anodes [5, 6]. Colloidal media (liquid crystalline [7] and micellar phases, microemulsions) were used as structure directing agents for electrodeposition.

Materials and Methods

The three-dimensional supports employed in the present work were: reticulated vitreous carbon (RVC, Electrolytica Inc., 39 pores per centimeter, thickness $2x10^{-3}$ m), uncompressed graphite felt (UGF, Test Solutions, thickness $3x10^{-3}$ m**)** and Ti mesh (VWR Canlab, thickness $2x10^{-4}$ m). Three colloidal media was investigated and compared as nanostructure forming agent during electrodeposition: cyclohexane based microemulsion and two micellar solutions (Triton X-100/isopropanol and Triton X-102, respectively). The aqueous phase contained 0.25-0.75 mM concentrations of H_2PtCl_6 and $(NH_4)_2RuCl_6$.

Results and Discussion

Electrodeposition from the Triton X-100/isopropanol micellar media generated a meso-porous PtRu structure on the RVC, UGF and Ti mesh supports with a Pt:Ru atomic ratio of 4:1. The resulting electrocatalytic activity toward methanol oxidation was the highest for PtRu/RVC followed by PtRuGF and PtRu/Ti_mesh [5]. Comparing the Triton X-100/isopropanol and Triton X-102 templating environments (Table I), it was found that Triton X-102 was beneficial for controlling the active crystallographic features of the Pt. The fraction of Pt [1,1,1] and [3,1,1], which are the most active planes for methanol electro-oxidation, has been increased (Table I).

Table I. Effect of colloidal media on the crystallographic features of the electrodeposited PtRu supported on graphite felt (UGF). Conditions: 20 A m^{-2}; 120 min and 341 K. Aqueous phase: 0.25 mM H_2PtCl_6 and 0.25 mM $(NH_4)_2RuCl_6$.

Pt Miller indices	5 vol% Triton X-100 / 20 vol% Isopropanol	12.5 vol% Triton X-102
[1,1,1]	34.6%	39.7%
[1,0,0]	43.2%	27.6%
[1,1,0]	14.4%	17.1%
[3,1,1]	7.8%	15.5%

In DMFC experiments the Pt-Ru (4:1 at. ratio)/GF anode with 1 mg cm^{-2} PtRu load, generated a peak power density of 74.1 mW cm^{-2} at 333 K. Under identical operating conditions commercial catalyst coated membrane (CCM) and catalyst coated diffusion layer (CCDL) anodes with 4 mg cm^{-2} PtRu (1:1 at. ratio), provided peak power densities of only 70.3 mW cm^{-2} and 27.8 mW cm^{-2}, respectively. In direct formic acid fuel cell (DFAFC) experiments at 333 K and 1 M HCOOH concentration, the maximum power density using the Pt-Ru (1 mg cm^{-2})/GF anode reached 86 mW cm^{-2}, compared to 52.6 mW cm^{-2} with CCM [6].

Significance

High-performance anodes for direct methanol and formic acid fuel cells were developed, by controlling the electrodeposited catalyst nanostructure and crystallographic features on three-dimensional supports, creating an extended reaction zone for electro-oxidation. In case of similar peak power output, this approach led to a four times reduction of the PtRu catalyst load (to 1 mg cm^{-2}) compared to commercial catalyst coated membranes, hence, facilitating the potential for commercialization of DMFCs.

References

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