Research Paper

Volume : 4 | Issue : 11 | November 2015 • ISSN No 2277 - 8179

Oxygen Reduction Reaction in The Presence of Methanol Using CoFeRu Electrocatalyst

Engineering

KEYWORDS : Electrocatalyst, ORR, microwave, CoFeRu.

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ABSTRACT

Investigations in direct methanol fuel cell (DMFC) have increased the demand for fundamental information about the behavior of the cathode electrocatalyst. Typically electrocatalyst (Pt) used for the oxygen reduction is rapidly poisoned due to the methanol crossover effect. For this reason, it is necessary to search lower cost and long useful life time electrocatalyst. CoFeRu was synthesized by microwave method at 180°C for 30 minutes. SEM morphology showed agglomerates of particles of different size. The EDS analysis showed few atomic percentage elements content (Co, Fe, Ru). According to X-ray diffraction the trimetallic CoFeRu phase is not observed. Electrochemical characterization demonstrated that the electrocatalytic activity of CoFeRu toward ORR is not affected by the methanol presence (1 and 2 mol L^{-1}). CoFeRu could be an excellent electrocatalyst as cathode in DMFC.

INTRODUCTION

The direct methanol fuel cell (DMFC) has an application as power sources for stationary and portable (mobile) applications [1]. However, there are barriers for this energy conversion device, principally in polymeric membrane and electrode materials. For reducing oxygen molecule at cathode in DMFC is necessary a higher overpotential which significantly lowers the cell efficiency and power density [2]. Another problem is the poisoning of the cathode by the methanol crossover effect [3]. The composition, porosity, morphology, structure, particle size, crystallographic orientation and activity of an electrocatalyst could be controlled selecting an effective synthesis method. Since some years ago, the thermal heating microwave synthesis has been an easy method to obtain electrocatalysts with good properties [4]. The present study is focused on the synthesized CoFeRu by microwave method using only water as solvent. Water is a good polar solvent, cheap, available, non-toxic, non-flammable, is also a potentially very useful solvent for microwave-mediated synthesis [5] and not generates waste polluting. Also was demonstrated that the electrocatalysts based on Co [6], Fe [7] and Ru [8] show attractive catalytic activity as cathode in a DMFC.

EXPERIMENTAL

CoFeRu was synthesized mixing 67.5 mg $Co(NO_3)_2•6H_2O$, 64.4 mg $FeCl_3•6H_2O$ and 50 mg $Ru_3(CO)_{12}$ with 10 ml of deionized water (18.2 MΩ cm) in a Synthos 3000-Anton Paar microwave reactor at 180°C for 30 minutes. The powder was filtered, washed and dried at vacuum all night. All reagents were Sigma-Aldrich grade. The surface morphology and Energy Dispersive X-ray Spectroscopy (EDS) analysis of CoFeRu electrocatalyst were investigated with a JEOL JSM-7800f. Rigaku DMAX-2200 diffractometer with a Jade 6.5 software was used by XRD.

Electrochemical characterization

Catalytic ink

Catalytic ink for the working electrode (Rotating Disk Electrode, RDE) was prepared using CoFeRu (30 wt%) supported on Vulcan® XC-72R with 15 µL of Nafion® solution (ElectroChem). 5 µL of the resulting ink was deposited on the disk electrode (0.1963 cm^2). After that, the electrocatalyst was characterized using a three compartments electrolytic cell, 0.5 mol L^{-1} H_2SO_4 (J.T. Baker) was used as electrolyte, a carbon rod and mercury/mercurous sulfate (Hg/Hg_2SO_4/0.5 mol L^{-1} H_2SO_4, 0.68 V vs. NHE) were used as counter and reference electrodes, respectively. A bipotentiostat (Pine Instrument, model AFCBP1), rotating control (Pine Instrument, model 616A) and Aftermath software were used to carry on electrochemical experiments. For the ORR experiments, the electrolyte was saturated with O_2 (Infra; UHP) for 30 minutes, before linear scan voltammograms (LSV). LSV curves were obtained from the oxygen open circuit potential $(E_{OC}^{O_2})$ to 0 V vs. NHE at 5 mV s^{-1} rate, under rotating conditions (100-900 rpm). This analysis also was studied in CH_3OH presence (1 and 2 mol L^{-1}, J.T. Baker), under the same conditions mentioned above.

RESULTS AND DISCUSSION

Scanning Electron Microscopy

SEM back-scattered electron image of CoFeRu is shown in Fig. 1. It can be seen that the electrocatalyst is well dispersed with agglomerates of particles of irregular and different size; where the brightest areas are attributed to the larger atoms (Ru, 101.07 g mol^{-1}). Smaller atoms are the other components, principally iron (55.845 g mol^{-1}).

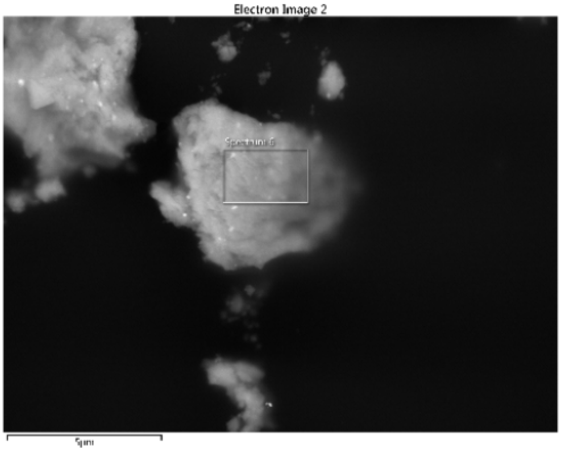

Figure 1: Back-scattering electron of the CoFeRu.

EDS Analysis

The EDS spectra showed dispersive peaks of oxygen (77.39 % At), carbon (2.22 %At), nitrogen (11.25 % At) and chlorine (0.86 % At), which come from the precursor reagents. The atomic ratios of Co:Fe:Ru are 0.06:4.39:3.83, respectively. The content of these metals are very low and it is in agreement with the x-ray diffraction patterns in Fig. 2, where cobalt phase is not observed.

XRD

XRD pattern of CoFeRu electrocatalyst is presented in Fig. 2. This diffractogram does not show crystallographic peaks well defined, only was observed a crystalline phase of $FeCl_2$ (Lawrencite) formed in 35.241°/(104), with a crystal size around of 10.7 nm. Also is observed some signals that could be attributed to Ru and Fe_2O_3 nanometric size presence, but due to the size was difficult to corroborate with XRD pattern.

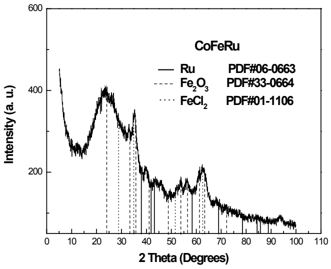

Figure 2: Diffractogram of CoFeRu.

Oxygen reduction reaction

ORR in aqueous solution can occur by two reaction mechanisms: a) via 4e$^-$ where the O_2 is directly reduced to produce water or b) via 2e$^-$ when the O_2 first produce H_2O_2 and after water, spending more potential. Both processes depend by the interaction of O_2 with the electrocatalyst surface and the type of molecular chemisorption (adsorption or protonation) [9]. Using the RDE technique can be studied qualitatively which reaction is carry on over the electrode surface. Current signal measured at the disk electrode is ruled by the kinetic and mass-transport. This category of RDE experiment is usually called a Koutecky-Levich experiment [10, 11]. According to Fig. 3a, CoFeRu shows activity for the ORR, the current densities and the $E_{OC}^{O_2}$ are stables, these values does not decrease by the methanol presence, with this behavior is clear that CoFeRu electrocatalyst is tolerant to the methanol presence. It is also observed in Fig. 3b, that the experimental lines are closer to 4e$^-$ transfer than 2e$^-$ transfer.

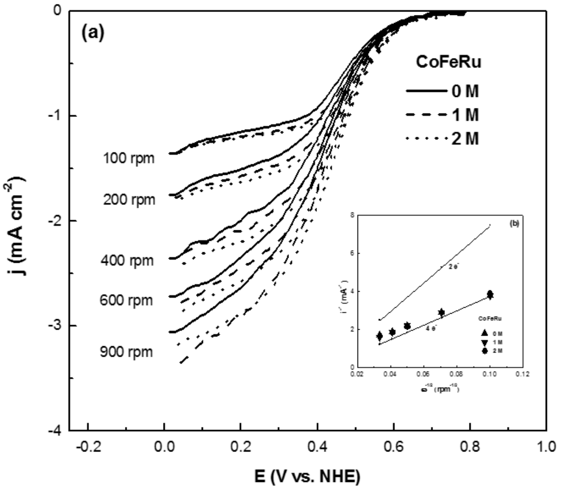

Figure 3: (a) Polarization curves for ORR and (b) experimental (at 0.24 V *vs.* NHE) and theoretical (2 and 4 e$^-$, solid lines) Koutecky-Levich plots of the CoFeRu in the absence and presence of 1 and 2 mol L^{-1} CH_3OH in O_2 saturated 0.5 mol L^{-1} H_2SO_4, the sweep rate was 5 mV s^{-1}.

Butler-Volmer equation has been the standard approach in macroscopic modeling of electrochemical kinetics in porous electrodes [13]. Table 1 summarizes the $E_{OC}^{O_2}$ and the electrokinetic parameters (*Tafel slope*, *b*; *transfer coefficient*, *α*; and the *exchange current density*, j_0) obtained from Tafel plots. It can be observed that the Tafel slope for the CoFeRu synthesized using deionized water as solvent is closer to 120 mV dec^{-1} than the material reported in the literature, indicating that a single electron exchange is involved in the rate-determining step [14]. The electrocatalyst also showed α values closer to 0.5 than CoFeRu($FeSO_4$). The j_0 for CoFeRu is two orders of magnitude smaller than CoFeRu($FeSO_4$), which could be attributed to the iron oxides presence [15]. The open circuit potentials ($E_{OC}^{O_2}$) are similar for both materials, even in the presence of methanol.

Table 1. Methanol concentration, $E_{OC}^{O_2}$ and electrokinetics parameters in absence and presence of 1 and 2 mol L^{-1} CH_3OH of the CoFeRu electrocatalyst compared with CoFeRu($FeSO_4$) [15].

Electrocatalysts	CH_3OH [mol L^{-1}]	$E_{OC}^{O_2}$ (V *vs.* NHE)	b (mV dec^{-1})	α	j_0 (mA cm^{-2})
CoFeRu ($FeSO_4$)	0	0.782	193	0.306	2.49 x 10^{-4}
	1	0.780	203	0.306	3.20 x 10^{-4}
CoFeRu ($FeCl_3$)	0	0.769	138	0.392	4.35 x 10^{-6}
	1	0.783	131	0.412	3.15 x 10^{-6}
	2	0.788	133	0.406	8.10 x 10^{-6}

CONCLUSIONS

CoFeRu synthesized in deionized-water by a thermal heating microwave method showed in general a better electrocatalytic behavior than the material synthesized with a mixture of deionized-water/ethylene-glycol as solvent. Therefore, the use of organic solvents with this synthesis method is avoided. Another important feature is its tolerance to the presence of methanol during the ORR. The electrocatalyst could be used as cathode in a Direct Methanol Fuel Cell.

ACKNOWLEDGMENTS

The authors are grateful to the DGAPA-UNAM for Antonia Sandoval González´s postdoctoral grant. This work was supported by the projects: PAPIIT-IA104415-UNAM and CONACYT-224366. We would like to thank Maria Luisa Ramón, Pedro Mexia Hernández, Abimael Mexia Hernández and Diego Quiterio Vargas, for valuable technical assistances.

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