Effect of addition of rhenium to Pt-based anode catalysts in electro-oxidation of ethanol in direct ethanol PEM fuel cell

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ABSTRACT

Breaking of C–C bond at low temperature to completely oxidize ethanol in direct ethanol fuel cell (DEFC) is the limiting factor for the development of DEFC as alternative source of power in portable electronic equipment. Binary and ternary Pt based catalysts with addition of Re, Pt–Re/C (20:20), Pt–Sn/C (20:20), Pt–Re–Sn/C (20:10:10) and Pt–Re–Sn/C (20:5:15) catalysts were prepared from their precursors by co-impregnation reduction method to study electro-oxidation of ethanol in DEFC. The electrocatalysts characterized by transmission electron microscope, scanning electron microscope, energy dispersive X-ray, and X-ray diffraction shows the formation of above mentioned bi- and tri-metallic catalyst with size ranges from 6 to 16 nm. Electrochemical analyses by cyclic voltammetry, linear sweep voltammetry and chronoamperometry show that Pt–Re–Sn/C (20:5:15) gives higher current density compared to that of Pt–Re/C (20:20) and Pt–Sn/C (20:20). The addition of Re to Pt–Sn/C is conducive to electro-oxidation of ethanol in DEFC. The power density obtained using Pt–Re–Sn/C(20% Pt, 5% Re, 15% Sn by wt) (30.5 mW/cm^2) as anode catalyst in DEFC is higher than that for Pt–Re–Sn/C(20% Pt, 10% Re, 10% Sn by wt) (19.8 mW/cm^2), Pt–Sn/C (20% Pt, 20% Sn by wt) (22.4 mW/cm^2) and Pt–Re/C (20% Pt, 20% Re by wt) (9.8 mW/cm^2) at 100 °C, 1 bar, with catalyst loading of 2 mg/cm^2 and 5 M ethanol as anode feed.

1. Introduction

In recent years a lot of research in the field of proton exchange membrane (PEM) fuel cells is focused on Direct ethanol fuel cells (DEFCs) due to ethanol's intrinsic advantages such as its non-toxicity, less volatility than methanol and renewability with high energy density (8.0 kWh/kg). Furthermore its easy production in large quantities by fermentation from sugar containing agricultural wastes adds up to its advantages. Bigger molecular size of ethanol than methanol helps in limiting the crossover through membrane from anode side to cathode. Despite certain advantages of ethanol in direct fuel cell, the development of DEFC is limited because of difficulty of C–C bond breaking at low temperature to completely oxidize ethanol [1–5]. The improvement in activity of anode electrocatalyst to break C–C bond of ethanol at lower temperature is essential as perfluorosulphonic acid based proton exchange membrane is used as solid polymer electrolyte. Platinum based bimetallic catalyst found to be most suitable anode electrocatalyst for the oxidation of alcohols [6]. Pure platinum is poisoned by strongly adsorbed species like CO, which is generated from the dissociation of organic molecules and thus the reactivity of platinum reduces [7]. One of the ways to improve catalytic activity is to add co-catalyst with platinum, which results in adsorption of OH$_{ads}$ species at a lower potential. The OH$_{ads}$ species help to oxidize CO to

CO_2 [3]. The platinum based alloy such as Pt—Ru [8—10], Pt—Sn [10,11], Pt—Mo [12], Pt—Pd [10] were reported as catalysts for electro-oxidation of ethanol. Out of these, Pt—Sn as anode electrocatalyst results in best performance of DEFC [11]. Sn is able to adsorb water molecules dissociatively to form OH_{ads} species, resulting in formation of CO_2 and CH_3COOH at lower potentials than Pt by oxidation of adsorbed CO and CH_3CO species, according to the bi-functional mechanism [12]. Sn is suggested to modify the electronic structure of Pt by forming an alloy with it, which improves ethanol oxidation reaction activity of the catalyst [10,11]. The addition of third metal to bimetallic electrocatalyst, which helps in C—C breakage at low temperature, may lead in complete oxidation of ethanol. In heterogeneous catalyses, rhenium is known to be a good catalyst for C—C bond breakage [13]. Moreover, in the reforming and cracking operations of petroleum fraction, Re has been found effective in breaking the C—C bond [14,15]. In this study Pt/C (40), Pt—Sn/C (20:20), Pt—Re/C (20:20), Pt—Re—Sn/C (20:10:10) and Pt—Re—Sn/C (20:5:15) catalysts were prepared by co-impregnation reduction method from their precursors to study ethanol electro-oxidation. The prepared electrocatalysts are characterized using transmission electron microscope (TEM), scanning electron microscope (SEM), energy dispersive X-ray (EDAX) and X-ray diffraction (XRD) analysis. Ethanol electro-oxidation in the presence of above catalysts is studied using cyclic voltammetry (CV), chronoamperometry (CA), linear sweep voltammetry (LSV). Finally, the catalysts are tested as anode in direct ethanol fuel cell. The results obtained are analyzed in the light of performance of DEFC.

2. Experimental

2.1. Material

The precursors used for the preparation of electrocatalysts were $H_2PtCl_6.6H_2O$ (Alfa Aesar, USA), $SnCl_2.2H_2O$ (Merck, Germany) and $ReCl_3$ (Alfa Aesar, USA). Vulcan XC-72 (Carbot, USA) was used as support for the catalysts. Carbon paper (90T, Toray, USA) was used as substrate for the catalyst powder to prepare the electrodes. Nafion® (DE 521, DuPont, USA) dispersion was used to make the catalyst slurry. Ethanol (Merck, Germany) and H_2SO_4 (Merck, Germany) were used as fuel and as electrolyte for electrochemical analysis, respectively. Nafion 117® (DuPont, USA) proton exchange membrane
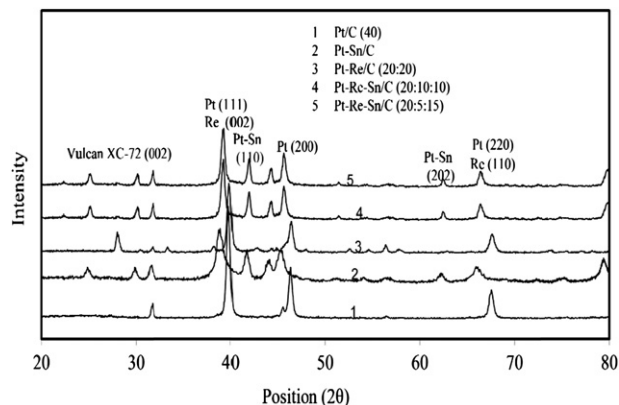

Fig. 1 — XRD patterns of Pt/C (40), Pt—Re/C (20:20), Pt—Sn/C (20:20), Pt—Re—Sn/C (20:10:10) and Pt—Re—Sn/C (20:5:15) catalysts.

was used to prepare membrane electrode assembly for DEFC. Pt/C (40%wt) (Johnson Matthey) was used as cathode catalyst.

2.2. Catalyst preparation

The precursors were first suspended in propanol and then ultrasonicated for 3 h. High-surface-area carbon black, e.g., Vulcan XC-72, was preheated to 110 °C and suspended in propanol separately and ultrasonicated for 3 h. Precursor suspension is then added drop wise to carbon suspension [17]. The weight ratio of Pt—X/C (X = Sn, Re, Re—Sn) was controlled according to the targeted metal loading. Ultrasonic blending for 3 h, of precursor and carbon suspension was carried out to ensure the proper impregnation of metal precursors on carbon support. The suspension is then kept at 70 °C for 12 h and all the propanol is evaporated. The precursor mixtures were reduced in hydrogen atmosphere at different temperatures to obtain desired bimetallic and tri-metallic catalysts by impregnation method. Table 1 shows different catalysts and their loadings. Abbreviation used to show the metal composition in the catalyst, e.g., Pt—Re—Sn/C (20:5:15) represents 20% Pt, 5% Re, 15% Sn by wt and rest 60 %wt is carbon.

2.3. Physical characterization

The morphology of the dispersed catalysts was examined by SEM (EVO 50, Zeiss UK) and TEM (CM 12, Philips, and The Netherlands). The particle size distribution and mean particle

Table 1 — The different bimetallic and tri-metallic combinations of catalysts prepared with different metal compositions.

Catalysts prepared	Percentage by wt.			
	Pt	Re	Sn	C
Pt/C	40	—	—	60
Pt—Re/C	20	20	—	60
Pt—Sn/C	20	—	20	60
Pt—Re—Sn/C	20	10	10	60
Pt—Re—Sn/C	20	5	15	60

Table 2 — The lattice parameter and the mean particle size obtained at Pt (1 1 1) diffraction peak of different catalysts.

Catalyst	2θ (°)	d- value (nm)	Lattice parameter	Particle size (nm)
Pt/C (40)	39.77	0.2264	0.392	9.3 ± 0.5
Pt—Re/C (20:20)	39.85	0.2260	0.400	16.9 ± 0.4
Pt—Sn/C (20:20)	38.93	0.2311	0.390	7.65 ± 0.5
Pt—Re—Sn/C (20:10:10)	39.27	0.2292	0.398	9.7 ± 0.6
Pt—Re—Sn/C (20:5:15)	39.25	0.2243	0.397	7.5 ± 0.7