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Bi-metallic and tri-metallic Pt–Sn/C, Pt–Ir/C, Pt–Ir–Sn/C catalysts for electro-oxidation of ethanol in direct ethanol fuel cell

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ABSTRACT

In the present work, combination of bi-metallic and tri-metallic Pt, Ir, Sn electro-catalysts was prepared by impregnation reduction method on carbon Vulcan XC-72 to improve upon electro-oxidation of ethanol in direct ethanol fuel cell. The prepared electro-catalysts were characterized by means of scanning electron microscope (SEM), transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD) analyses. XRD and TEM analyses reveal that the prepared catalysts are of nano size (6–10 nm) range. It is shown that Pt lattice parameter decreases with the addition of Ir, and increases with the addition of Sn in Pt–Ir–Sn/C catalyst. The electro-catalytic activities characterized by cyclic voltammetry (CV), linear sweep voltammetry (LSV) and chronoamperometry (CA) techniques reveal that the addition of small amount of Ir in Pt–Sn/C electro-catalyst exhibits higher activity towards ethanol oxidation than the Pt–Sn/C (20% Pt and 20% Sn by wt) electro-catalyst. The single direct ethanol fuel cell (DEFC) test at 90 °C, 1 bar with catalyst loading of 1 mg/cm² and 2 M ethanol as anode feed showed an enhancement of catalytic activity in following order: Pt–Ir–Sn/C (20% Pt, 5% Ir and 15% Sn by wt) > Pt–Ir–Sn/C (20% Pt, 10% Ir and 10% Sn by wt) > Pt–Sn/C (20% Pt and 20% Sn by wt) > Pt–Ir–Sn/C (10% Pt, 15% Ir and 15% Sn by wt) > Pt–Ir/C (20% Pt and 20% Ir by wt) > Pt/C (40% Pt by wt). Pt–Ir–Sn/C (20% Pt, 5% Ir and 15% Sn by wt) exhibited highest performance among all the catalysts prepared with power density of 29 mW/cm² in DEFC operating at 90 °C.

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1. Introduction

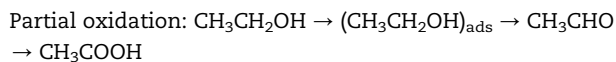
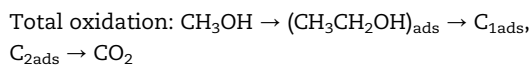
Complete electro-oxidation of ethanol at low temperature (below 100 °C) would enhance the commercialization prospect of direct ethanol fuel cell (DEFC) compared to that direct methanol fuel cell. Use of ethanol as fuel has distinctive advantage over methanol. Ethanol as a fuel has higher theoretical mass energy density than methanol (8 vs. 6.1 kWh/kg)

and is relatively non toxic. The complete electro-oxidation of ethanol involves 12 electrons and breaking of C–C bond in contrast to methanol electro-oxidation, which involves only 6 electrons. However, for small scale applications, such as powering electronic devices or as a sensor in breathalyzers, the DEFC durability and reliability are the main requirements. Ethanol oxidation in acid media occurs with the adsorption of acetyl species and the formation of stable intermediate

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products such as acetaldehyde and acetic acid. Following reaction scheme is proposed for ethanol electro-oxidation [1].



where $\text{C}_{1\text{ads}}$ and $\text{C}_{2\text{ads}}$ represent the adsorbed intermediates with one and two carbon atoms, respectively. Carbon supported Pt–Sn based catalysts for electro-oxidation of ethanol are well known in the context of DEFC. On the Pt-sites adsorption and decomposition of ethanol take place and dissociative adsorption of water occurs on the Sn-sites. During the dissociative adsorption of ethanol on Pt-sites, Sn provides the O-species for the oxidation of CO-like species [2–4]. Jiang et al. [3] prepared Pt–SnO₂ alloy by polyol method, which inhibited the hydrogen adsorption/desorption process. Cao et al. [5] showed that both Sn and Ir promote the electro-oxidation of adsorbed CO-like species. Ir₃Sn/C shows higher rate of ethanol oxidation than Pt₃Sn/C in a low potential region at 90 °C [5]. Electro-oxidation of ethanol on Ir was also investigated by de Tacconi et al. [6] and found that oxidation of Ir is selective and produces high percentage of acetic acid. Calegario et al. [7] used IrO₂ on Pt as modifiers for better electro-catalytic activity towards ethanol. Chen et al. [8] showed higher rate of methanol oxidation by using IrO₂ on Pt. Ioroi et al. [9,10] used Ir and IrO₂ in DEFC to stabilize the Pt–Sn/C. Ribeiro et al. [11] developed various compositions of Pt–Sn–Ir/C catalyst by thermal decomposition method. It was shown that the composition of Pt₆₈Sn₉Ir₂₃/C has highest durability and activity for ethanol oxidation. In this study Pt/C, Pt–Sn/C, Pt–Ir/C and Pt–Ir–Sn/C catalysts were prepared by impregnation reduction method from their precursors to study ethanol electro-oxidation. We believe that impregnations reduction method would result in formation of uniform bi-metallic and tri-metallic catalysts and will improve ethanol electro-oxidation in DEFC. The prepared electro-catalysts were characterized using transmission electron microscope (TEM), scanning electron microscope (SEM), energy dispersive X-ray (EDX) and X-ray diffraction (XRD) analyses. Ethanol electro-oxidation of all the prepared catalysts was studied using cyclic voltammetry (CV), linear sweep voltammetry (LSV), chronoamperometry (CA), dynamic hydrogen electrode (DHE) and in DEFC to check cell performance.

2. Experimental

2.1. Material

The precursors used to prepare anode electro-catalysts were H₂PtCl₆.6H₂O (Alfa Aesar, USA), SnCl₂.2H₂O (Merck, Germany) and H₂IrCl₆.xH₂O (Alfa Aesar, USA). Vulcan XC-72 (Carbot, USA) was used as support for the catalysts. Carbon paper (90T, Toray, USA) was used as gas diffusion layer in single cell test and to prepare the working electrodes in half cell analysis. Nafion® (DE 521, DuPont USA) dispersion was used to make

the catalyst ink. Ethanol (Merck, Germany), Iso-propanol (Merck, Germany), and H₂SO₄ (Merck, Germany) were used as fuel and electrolyte for electrochemical analysis. The solid electrolyte used in DEFC was Nafion 117® from DuPont USA.

2.2. Catalyst preparation

Several carbon supported platinum based bi-metallic and tri-metallic catalysts such as Pt–Ir/C, Pt–Sn/C and Pt–Ir–Sn/C were prepared by impregnation reduction method. Table 1 shows different catalyst combinations prepared. In impregnation reduction method, the metal precursors were first suspended in iso-propanol by ultrasonicated for 3 h. High-surface-area carbon black, e.g., Vulcan XC-72, was preheated to 110 °C for 2 h and suspended in iso-propanol separately by ultrasonication for 3 h. Precursor suspension is then added drop wise to carbon slurry. The weight ratio of Pt–X/C (X = Sn, Ir, Ir–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 was then kept at 70 °C for 12 h to evaporate iso-propanol. The dry precursor mixtures obtained were reduced in continuous supply of hydrogen gas in a tubular furnace for 4 h at temperatures according to temperature programmed reduction to obtain desired bi-metallic and tri-metallic catalysts.

2.3. Physical characterization

The morphology of the dispersed catalysts was examined by SEM (EVO 50, Zeiss UK) and TEM (CM 12, Philips, Netherlands). The particle size distribution and mean particle size were evaluated using TEM. XRD patterns were recorded by means of XRD (PW 3040/60, X'Pert PRO, Netherlands) with an area detector using a Cu K α radiation source ($\lambda = 1.54056 \text{ \AA}$) to study the crystal structure and detect the alloy formation. The mean particle size analyzed from TEM is verified by determining the particle size from XRD pattern using Scherer's formula. The tube voltage and current were maintained at 40 kV and 40 mA, respectively. The 2θ angles ranging from 20° to 80° were explored at a scan rate 5° min⁻¹. EDX was carried out using scanning electron microscope (EVO 50, Zeiss UK).

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

Catalysts prepared	Percentage by wt.			
	Pt	Ir	Sn	C
Pt–Ir/C	20	20	–	60
Pt–Sn/C	20	–	20	60
Pt–Ir–Sn/C	20	10	10	60
Pt–Ir–Sn/C	10	15	15	60
Pt–Ir–Sn/C	20	5	15	60

Abbreviations such as (20:20), (20:10:10) are used to show the metal composition by wt. e.g. Pt–Ir–Sn/C (10:15:15) represents 10% Pt, 15% Ir, 15% Sn by wt rest 60% is carbon.

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