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# Effect of support materials on the performance of direct ethanol fuel cell anode catalyst



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## ABSTRACT

Pt–Ru catalysts supported on mesoporous carbon nitride (MCN), multiwall carbon nano tubes (MWCNTs), treated MWCNTs (t-MWCNTS) and Vulcan-XC were prepared using co-impregnation reduction method for the oxidation of ethanol in direct ethanol fuel cell (DEFC) to study the effect of support material. The MCN support was prepared using SBA-15 as template and t-MWCNTs were prepared by refluxing in HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> mixture (1:3) using MWCNTs. XRD shows the formation of Pt–Ru bi-metallic catalyst with size ranges from 7 to 17 nm using different supports. The catalyst and its supports were characterized by physically and electrochemically. Linear sweep voltammetry, cyclic voltammetry and chrono amperometry studies of the above systems reveal that MCN supported Pt–Ru catalyst shows higher electro-catalytic activity towards ethanol oxidation compared to Pt–Ru in treated t-MWCNTs, MWCNTs and Vulcan-XC supports. The performance of DEFC based on maximum power density is found to be in the order Pt–Ru/MCN > Pt–Ru/t-MWCNTs > Pt–Ru/MWCNTs > Pt–Ru/Vulcan-XC. The Pt–Ru/MCN shows highest power density of 61.1 mW cm<sup>-2</sup> at 100 °C, 1 bar pressure with catalyst loading of 2 mg cm<sup>-2</sup> using 2 M ethanol feed.

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## 1. Introduction

Direct ethanol fuel cells (DEFCs) have been of great interest as power sources for mobile, stationary and portable applications. However, the complete oxidation of ethanol to CO<sub>2</sub> is tough due to the difficulties in C–C bond breaking and the formation of CO-intermediates that poison the platinum anode catalysts [1–3]. The activity of a catalyst for ethanol electro-oxidation depends on the particle size distribution and dispersion of catalyst and closely linked to the characteristics of the support used [4]. In order to increase the electro catalytic activity of Pt towards ethanol oxidation, different alloys with a second metal such as Ru, Sn, Ir, Re, or Mo have been employed. Among the binary Pt-based catalysts, Pt–Sn and Pt–Ru pairs are most

prospective because of its better capability of handling CO poisoning. In contrast to the improved catalytic activity of Pt–Sn bimetallic catalysts, the selectivity for CO<sub>2</sub> formation generally remained very low [5]. For all catalysts, incomplete ethanol oxidation to C<sub>2</sub> products (acetaldehyde and acetic acid) prevails, CO<sub>2</sub> formation contributes to ≤1%, in particular, in low potential region [6], which is of our interest. Using catalyst support has been proven as an effective approach to lowering the usage of noble metal and simultaneously improving the catalytic activity by incorporating relatively large surface area, good electrical conductivity, and an accessible porosity [7]. Carbon black having high conductivity and high surface area has been widely used as catalyst support for fuel cells to ensure large electrochemical reaction surface [8–15]. Over last decades large number of other carbonaceous and non-carbonaceous

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support materials has been studied [11]. To deal with the issue of carbon corrosion non-carbonaceous support materials like titania, indium oxide, alumina, silica, tungsten oxide, and conducting polymers have been investigated [10]. Materials like ceria [10] and zirconia [8,9] have also been explored. Carbonaceous support materials like mesoporous carbon, carbon nanotubes (CNTs), nanodiamonds, carbon nanofibres (CNF) and graphene possess a property like high surface area, high electrical conductivity and relatively good stability in acid and alkaline medium. CNTs [12,13], hollow nano spheres [16] and carbon nano fibers (CNF) [17], have proven to be effective as supports for anode electro catalysts. CNTs have excellent electrical conductivity but they have poor pore development and low surface area compared to Vulcan-XC [18]. Multiwall carbon nanotubes (MWCNTs) are made of a series of single-walled CNTs arranged coaxially with regularly increasing diameter. MWCNTs are usually long, tangled together and have closed ends [19], which limits the application of MWCNTs. Thus, it is very important to purify and oxidize the surface of MWCNTs. Treatment of the MWCNTs in nitric acid results in presence of carboxylic acid groups ( $-\text{COOH}$ ) on the surface of MWCNTs and it would shorten and unbundle [19]. Short and functionalized MWCNTs results in the increase of defects and surface area, which makes a promising starting point for the application of MWCNTs as metal catalyst support in DEFC.

Carbon nitride (CN) is a material of great interest due to its incorporation of a nitrogen atom in the carbon structure which enhances energy storage, conduction, field-emission, mechanical properties [20]. Mesoporous carbon has high mesoporosity and relatively low microporosity, and has amorphous framework [21]. Mesoporous carbon nitride (MCN) materials [22] prepared from SBA-15 as template [21,22] have been receiving much attention, as they are used in size and shape selective adsorption media, chromatographic separation systems, catalysts, nano reactors, battery electrodes, capacitors, energy storage devices, and biomedical devices [20–22]. Therefore, it would be of great interest to develop MCN supported catalyst for the oxidation of ethanol in DEFC.

In this study Pt–Ru catalysts supported on MCN, MWCNTs, treated MWCNTs (t-MWCNTs) and Vulcan-XC were prepared and tested for ethanol oxidation. Pt–Ru based metal catalysts and their supports were physically characterized using fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), transmission electron microscope (TEM), thermo gravimetric analysis (TGA), and X-ray photoelectron spectroscopy (XPS) techniques. The linear sweep voltammetry (LSV), cyclic voltammetry (CV) and chrono amperometry (CA) tests were carried out. Finally, performance of membrane electrode assemblies (MEAs), using Pt/C as catalyst at the cathode and Pt–Ru as metal catalyst at anode with different supports, e.g., MCN, t-MWCNT, MWCNT and Vulcan XC were carried out in a  $5\text{ cm}^2$  MEA of DEFC.

## 2. Experimental

### 2.1. Material

Pt–Ru as anode catalyst on different supports, e.g., MCN, t-MWCNTs, MWCNTs and Vulcan-XC were prepared with the final metal loading of 40 wt% on 60 wt% support, using

MWCNTs (95% Alfa Aesar), SBA-15 (ACS material) template for MCN, metal precursor  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  (Alfa Aesar, USA), and metal precursor  $\text{RuCl}_3$  (Alfa Aesar, USA).  $\text{HNO}_3$  (Merck, Germany) was used for purification and surface oxidation of MWCNTs. Also Vulcan-XC72 (Carbot, USA), was used as support for Pt–Ru anode catalysts for comparison. Carbon Paper (toray 120) was used as gas diffusion layer in DEFC test. Nafion<sup>®</sup> (DE 521, DuPont, USA) dispersion was used to make the catalyst ink slurry. Ethanol (Merck, Germany), and  $\text{H}_2\text{SO}_4$  (Merck, Germany) were used as fuel and as electrolyte for electrochemical analysis, respectively. Nafion 117<sup>®</sup> (DuPont, USA) proton exchange membrane (PEM) was used as electrolyte to prepare MEA. Pt/C (40%wt) (Johnson Matthey) was used as cathode catalyst.

### 2.2. Acid treatment of MWCNTs

MWCNTs were purified by suspending 1 g of raw MWCNT, in 4 M  $\text{H}_2\text{SO}_4$  and 4 M  $\text{HNO}_3$  and ultra sonicated for 2 h [18]. Then, the mixture was refluxed at  $140\text{ }^\circ\text{C}$  for 14 h under vigorous stirring. Finally, the t-MWCNTs were diluted with water, filtered, washed with excess de-ionized (DI) water till pH is 7, and dried at  $50\text{ }^\circ\text{C}$  in a vacuum oven for overnight.

### 2.3. Synthesis of MCN as support

The MCN used as support of bimetallic Pt–Ru catalyst was synthesized using calcined mesoporous silica SBA-15 as a hard template. Mesoporous silica template (0.30 g) was added to a mixed solution containing 1.2 g of ethylenediamine (EDA) and 2.4 g of carbon tetrachloride (CTC) at room temperature [20–24]. The above solution was then stirred and refluxed at  $90\text{ }^\circ\text{C}$  for 10 h to induce polymerization of the precursor. The resulting dark-brown mixture was heat treated at  $400\text{ }^\circ\text{C}$  for 2 h in nitrogen flow to carbonize the polymer. After pyrolysis the MCN product was recovered by dissolution in 5 wt% HF aqueous solutions to remove the silica template. The final product was washed several times with ethanol and dried overnight at  $100\text{ }^\circ\text{C}$ .

### 2.4. Catalyst preparation

Pt–Ru metals were loaded on different supports, e.g., t-MWCNTs, MWCNT, MCN and Vulcan-XC using co-impregnation reduction method. A requisite amount of metal precursors  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  and  $\text{RuCl}_3$  were first suspended in iso-propanol by ultrasonication for 3 h. Different supports were preheated to  $70\text{ }^\circ\text{C}$  for 2 h and suspended in iso-propanol separately by ultrasonication for 3 h [25–28]. The weight ratio was controlled according to the targeted metal loading. Ultrasonic blending for 3 h of precursor and support suspension was carried out to ensure the proper impregnation of metal precursors on support. The suspension was then kept at  $70\text{ }^\circ\text{C}$  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  $400\text{ }^\circ\text{C}$  according to temperature programmed reduction to obtain desired bi-metallic catalysts.

### 2.5. Physical characterization

The morphology of the catalyst support was examined by TEM (CM 12, Philips, Netherlands). Before TEM measurements, the

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