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Enhanced oxygen reduction reaction activity through spillover effect by Pt–$Y(OH)_3$/C catalyst in direct methanol fuel cells

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ABSTRACT

Dynamic spillover of metal oxide aided by yttrium hydroxide through its altervalent nature is utilized to develop a new carbon supported Pt–$Y(OH)_3$ hybrid catalyst with varying Pt:Y atomic ratio of 1:1, 2:1 and 3:1 and characterized by X-Ray diffraction and Transmission electron microscopy techniques. Pt–Y/C catalysts exhibit significant improvement in oxygen reduction reaction (ORR) over commercial Pt/C. The effects of composition toward ORR with and without methanol have been studied. Among the various Pt–$Y(OH)_3$/C catalysts, the one with Pt to Y in 3:1 atomic ratio shows the highest activity for ORR in aqueous $HClO_4$ solution without methanol while the one with Pt to Y in 2:1 atomic ratio shows the maximum activity for ORR in presence of methanol. A direct methanol fuel cell (DMFC) employing carbon-supported Pt–$Y(OH)_3$ as the cathode catalyst delivers a peak-power density of 105 mW/cm^2 at 70 °C as compared to a peak-power density of 64 mW/cm^2 obtained with the DMFC employing carbon-supported Pt catalyst operating under similar conditions.

1. Introduction

Direct methanol fuel cells (DMFCs) have received substantial interest in recent years for their potential use as power sources for mobile applications. However, the DMFC performance is still hindered by several factors mainly, sluggish kinetics of both anode and cathode reactions and the crossover of methanol from the anode to the cathode through the proton exchange membrane, which are precluding their commercialization [1]. To address the crossover issue along with the improvement of cathode reaction kinetics, one strategy is to develop oxygen reduction reaction (ORR) electro-catalysts with high catalytic activity and good methanol tolerance [2]. Though carbon supported Platinum (Pt/C) is the most effective catalyst for ORR in polymer electrolyte fuel cell, it is not selective towards ORR in presence of methanol. In literature, higher methanol tolerance is reported for non-noble metal electro-catalysts based on macrocycles and chalcogenides of transition metals [3–7]. These electro-catalysts have shown nearly the same activity for ORR in the absence as well as in the presence of methanol. However, in methanol-free electrolytes, these materials did not reach the catalytic activity of dispersed platinum. The negative effect of methanol crossover on cell performance is mitigated by using Pt-based binary catalysts [2,8,9].

Recent work showed that the addition of yttrium to Pt increases the ORR activity of Pt [10–11]. A Pt_3Y alloy catalyst was reported as a promising ORR electro-catalyst. In the above studies, sputtering method was used for the preparation of Pt–Y alloy. Carbon supported Pt–Y alloy electro-catalyst is reported for ORR in polymer electrolyte fuel cell [12]. However, the procedure followed was precipitation of Yttrium during reduction of Pt precursor, followed by heating. The authors have compared the performance of the product obtained before and after annealing. On annealing the performance is reduced, which could be due to sintering of Pt.

The altervalent features of transition metal have been utilized to improve the catalytic activity of electro-catalysts through its dynamic spillover effect [13–16]. In particular transition metal oxides like TiO_2 and WO_3 have been used. The working principle of such metal oxide systems is based on the hydrophilic behavior due to water molecules trapped inside the oxide network turning to hydrous network, which substantially behaves as a continuous undisturbed reversible membrane mechanism of the altervalent changes resulting in OH^- transfer within the system with consequent spillover of primary oxide over metallic catalyst particle. Based on this lead, in the present study, Platinum–Yttrium hydroxide based catalyst supported on carbon is developed and evaluated for ORR activity in presence and absence of methanol. Desired atomic ratio of Pt to Y for ORR in presence and absence of methanol is also optimized through half-cell and cell polarization studies.

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2. Experimental

2.1. Preparation of Pt–Y(OH)$_3$/C catalyst

Carbon supported Pt–Y(OH)$_3$ (40 wt.%) catalysts containing Pt and Y in varying atomic weight ratio, namely 1:1, 2:1 and 3:1 were prepared by employing the conventional NaBH$_4$ reduction method. In a typical synthesis, $H_2PtCl_6 \cdot 6H_2O$ and $Y(NO_3)_3 \cdot 6H_2O$ were used as the Pt and Y precursors, respectively. The precursors were dissolved in a methanol and de-ionized (DI) water mixture and an appropriate amount of carbon (Vulcan XC72R) was dispersed in the solution. The mixture was stirred for 30 min. Subsequently, the temperature was raised to 80 °C followed by the addition of 0.25 M of NaBH$_4$ solution. The resulting mixture was further stirred for 1 h followed by filtering. The resulting solid was washed with DI water and dried.

2.2. Characterization of catalysts

The crystalline structure of the supported catalysts were studied by recording their X-ray powder diffraction (XRD) patterns between 20° and 80° in reflection geometry in steps of 5° min^{-1} using CuK$_\alpha$ radiation ($\lambda = 1.5406$ Å). This catalyst is also characterized by Fourier transform infrared (FT-IR) spectrometry. The composition analysis of the catalysts was performed with ICP-OES. The structure and morphology of electro-catalysts were characterized using a Transmission Electron Microscope (TEM), JEOL model 1200 EX, operating at an accelerating voltage of 120 kV.

Electrochemical measurements were performed in a conventional three-electrode cell using an electrochemical analyzer (Autolab PGSTAT-30). A saturated calomel electrode (SCE) and Pt foil were used as reference and counter electrodes, respectively. The ORR activity and methanol tolerant behavior of various Pt–Y(OH)$_3$ catalysts were studied using Rotating Disk Electrode (RDE) and compared with commercially available Pt/C (40%). The porous working electrodes were prepared as follows: 7.5 mg of supported catalyst, 10 wt.% of Nafion solution (DuPont, USA) and 1.5 ml of ultra pure water were mixed ultrasonically, and 20 μL of the suspension was quantitatively transferred to the surface of the freshly polished-glassy-carbon disk with a geometrical area of 0.071 cm^2. The electrode was dried at room temperature. Prior to any electrochemical measurement, the working electrode was cycled between −0.25 and 0.8 V vs. SCE at a sweep rate of 50 mV/s for removing contaminants from the electrode and activating it. Experiments were conducted in nitrogen-purged 0.5 M aq. HClO$_4$ solution. High-purity nitrogen and oxygen were used for de-aeration and aeration of the solutions, respectively. During the ORR measurements, the electrolyte was purged with a gentle flow of oxygen. The electrochemical durability of the high-performing catalyst namely, Pt–Y(OH)$_3$ was carried out by repeated cycling between −0.24 and 0.8 V vs. SCE for 1000 cycles. The linear sweep voltammograms were recorded before and after 1000 cycles to compare the change in half-wave potential. All experiments were carried out at 25 °C.

The catalysts were evaluated in DMFCs by making membrane electrode assemblies (MEAs) following the procedure described elsewhere [2]. The cathode catalyst layer comprised 1 mg$_{Pt}$/cm^2 and 30 wt.% Nafion while the anode catalyst layer contained Pt (40 wt.%)-Ru (20 wt.%)/C (Alfa Aesar) with a Pt loading of 2 mg/cm^2 and 10 wt.% Nafion. A thin layer of Nafion ionomer was applied to the catalyst surface of both the electrodes. The geometric area of all the MEAs used in the present study was 4 cm^2. MEAs were performance tested using a conventional fuel cell fixture with a parallel serpentine flow-field machined on graphite plates (Schunk Kohlenstofftechnic). The cells were performance tested at 70 °C with 2 M aq. methanol at a flow rate of 2 sccm at the anode side and oxygen at a flow rate of 200 sccm at the cathode side. The galvanostatic polarization data were recorded using an LCN100-36 electronic load procured from Bitrode Corporation, US. The reproducibility of the data was ascertained.

3. Results and discussion

Fig. 1(a) shows the powder XRD pattern of Pt–Y(OH)$_3$(2:1)/C catalyst. The diffraction patterns show the characteristics of highly crystalline face centered cubic (fcc) Pt, with peaks corresponding to (111), (200), and (220) planes. However, absence of characteristic yttrium peak in XRD suggests that it may be present in amorphous form. The average crystallite size calculated from XRD data using Scherrer equation is 8.4 nm. FT-IR spectra for the catalyst given in Fig. 1(b) shows a broad peak at 3321 cm^{-1} due to O–H stretching revealing Yttrium is present in the hydroxide form. The absorption frequency corresponding to –OH in IR could also come from functional

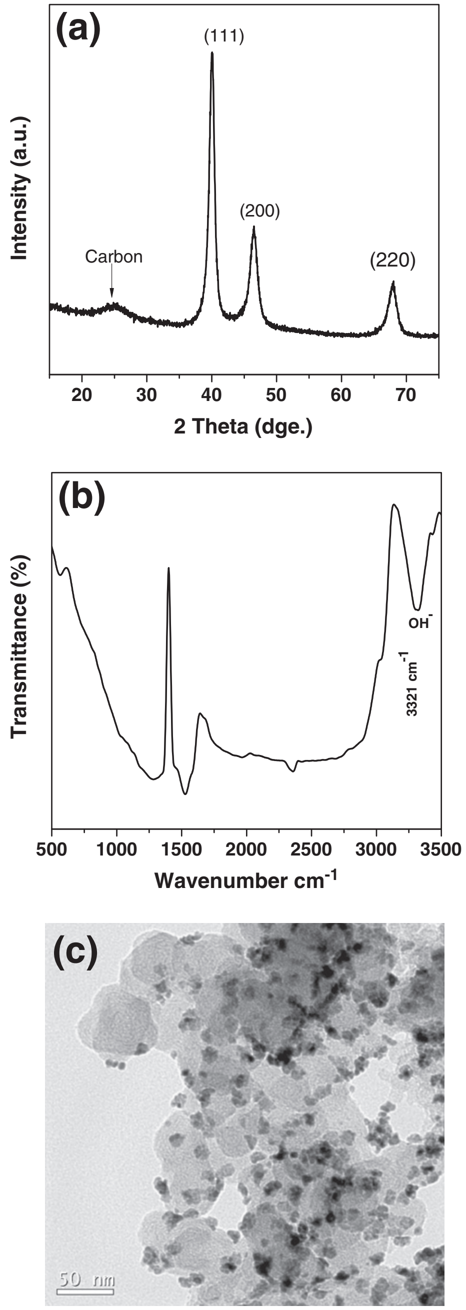

Fig. 1. (a) XRD pattern of Pt–Y(OH)$_3$ (2:1)/C catalyst, (b) FT-IR spectrum of Pt–Y(OH)$_3$/C and (c) TEM image for Pt–Y(OH)$_3$/C.