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Pd–TiO_2/C as a methanol tolerant catalyst for oxygen reduction reaction in alkaline medium

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ABSTRACT

TiO_2 on carbon was prepared by sol–gel method. Pd supported on TiO_2–C comprising Pd and Ti in varying atomic ratios namely, 1:1, 2:1 and 3:1 was prepared and characterized by X-ray diffraction and Transmission electron microscopy techniques. The electrocatalytic activity for oxygen reduction reaction in aqueous 0.1 M KOH solution containing methanol was characterized by rotating disk electrode. Catalytic activity of Pd–TiO_2(3:1)/C for ORR and methanol tolerance was found to be superior in relation to Pd/C.

1. Introduction

An alkaline fuel cell using an anion exchange membrane as an electrolyte is called alkaline polymer electrolyte membrane fuel cell (APEMFC) [1] and APEMFCs using methanol as fuel is referred as alkaline direct methanol fuel cells (ADMFCs) [2,3]. Methanol crossover in ADMFCs may not be completely eliminated though it is lesser than that in DMFCs [4]. Hence, the development of suitable methanol-tolerant non-Pt based electrocatalysts is desired.

Pd/C is a promising substitute for Pt/C because of its outstanding electro-catalytic activity for alcohol oxidation [5] and oxygen reduction reaction (ORR) [6–9] in alkaline medium, besides cost and availability. The modification of Pd with transition metals (M) (M = Ni, Co, Fe, V, and Ti) has resulted in higher electro-catalytic activity toward ORR than pure Pd [10]. Catalysts based on metal–transition metal oxide are known to improve the ORR activity and methanol tolerance. The hypo-d-electron transition metal oxides have high chemical-stability, good corrosion-resistance, and strong metal-support interaction, which can enhance the activity of the catalysts. They, as catalyst supports, are able to stabilize and disperse adequately a number of active phases, as well as to retain a high surface area [11]. Among different metal oxides, TiO_2 is attractive due to its promising electrochemical properties, chemical stability, non-toxic nature and when combined with carbon as catalyst support shows better catalytic activity than metal supported on TiO_2 [12] due to poor conductivity of the latter compared with carbon. Further, Pt–TiO_2/C shows improved stability in PEMFCs compared with Pt/C [13].

Recently, F. Hu et al. have shown better ethanol oxidation and stability for Pd supported on carbonized TiO_2 nanotube in alkaline medium compared with Pd/C [14]. Nguyen et al. investigated the ethanol oxidation on Pd/TiO_2 and Pd/Ti_nO_{2n-1} in alkaline medium and found Pd/Ti_nO_{2n-1} to be suitable. But Ti_nO_{2n-1} showed lower electronic conductivity than carbon [15]. Mentus et al. have reported higher ORR activity for Pd/TiO_2 in alkaline medium than in acidic medium [16]. Pioneering work on ORR activity of Pt-TiO_2 in alkaline medium was reported by of Temmeveski et al. [17]. To the best of our knowledge, only a few studies have been performed on Pd–TiO_2/C in alkaline medium, however, they do not cover the methanol tolerance behavior and also the optimum requirement of Ti.

In the present study, Pd–TiO_2/C comprising Pd and Ti in varying atomic ratios namely, 1:1, 2:1 and 3:1 were prepared, and evaluated for ORR in the presence of methanol.

2. Experimental section

2.1. Preparation of Pd–TiO_2/C

A sol–gel route was adopted to prepare TiO_2/C. The amount of Pd–TiO_2/C was fixed to be 1.0 g. Pd was fixed at 200 mg. Titanium isopropoxide and carbon were taken proportionately so as to have Pd:Ti in varying ratios of 1:1, 2:1 and 3:1 in the final catalyst. For example in the preparation of Pd–TiO_2 (3:1)/C, 190.26 mg of titanium isopropoxide was diluted with isopropanol and made into a homogeneous solution by ultrasonication. 50 μL of 0.1 M aqueous H_2SO_4 was added to titanium isopropoxide solution to make the titania sol and sonicated for half an hour followed by the addition of 734 mg of Vulcan carbon (XC72R) under stirring condition. To form a gel, the resultant mixture was left for

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12 h under stirring condition and heated up to 80 °C, for 1 h to remove all volatile substances present in it. The resulting TiO_2/C powder was ground.

The prepared TiO_2/C was suspended in deionized water and subjected to ultrasonication for 30 min and the resulting ink was added to the solution containing 333.32 mg of $PdCl_2$ with constant stirring followed by the addition of alkaline 0.5 M $NaBH_4$. The mixture was constantly stirred for 1 h, then filtered, washed with deionized water, and dried in an oven overnight at 80 °C. The prepared Pd–TiO_2/C containing Pd and Ti in varying atomic ratios namely, 1:1, 2:1 and 3:1 is designated and referred as Pd–TiO_2(1:1)/C, Pd–TiO_2(2:1)/C and Pd–TiO_2(3:1)/C, respectively.

2.2. Characterization of catalysts

X-ray diffraction (XRD) patterns were obtained on a PANalytical X-ray Diffractometer using CuK_α radiation ($\lambda = 1.5406$ Å) between 10° and 90° in reflection geometry in steps of 5° min^{-1}. The microscopic features of the samples were examined by using TECNAI 20 G2 TEM (200 kV).

All the catalysts were electrochemically characterized using Cyclic Voltammetry (CV) and ORR was evaluated based on the Liner Sweep Voltammetry (LSV) measurements. The electrochemical setup, the cell arrangement, preparation of electrodes and catalyst ink are the same as that is reported elsewhere [18]. 70 μg of Pd was loaded on glassy carbon disk (0.196 cm^2) which was used as a working electrode. A pre-calibrated silver–silver chloride (Ag/AgCl, 0.210 V vs. SHE) electrode and a platinized Pt foil were used as the reference and counter electrodes, respectively, in the three-electrode configuration. All electrochemical experiments were carried out at room temperature (~25 °C).

In order to clean and activate the working electrode, it was cycled between −1 and 0.5 V at a sweep rate of 50 mV/s in high pure nitrogen purged aqueous solution containing 0.1 M KOH and 0.1 M CH_3OH until stable and reproducible voltammograms were obtained. The CVs were recorded once the working electrode was well equilibrated. LSV experiments were performed using RDE in oxygen saturated aqueous solution. LSV data were recorded in the cathodic-sweep direction from 0.1 V to −0.5 V over a range of rotations (400 to 2400 rpm) at a scan rate of 3 mV s^{-1}.

3. Results and discussion

The crystalline structures of Pd–TiO_2/C comprising Pd and Ti in varying ratios are characterized by XRD and shown in Fig. 1(A). For comparative purpose, the XRD pattern of 20 wt.% of Pd/C is also included in the figure. The diffraction peaks at 2θ values of 40.1°, 46.68°, 68.08° and 82.0° are due to the (111), (200), (220) and (311), respectively for the crystalline planes of Pd/C with a face centered cubic (fcc) structure.

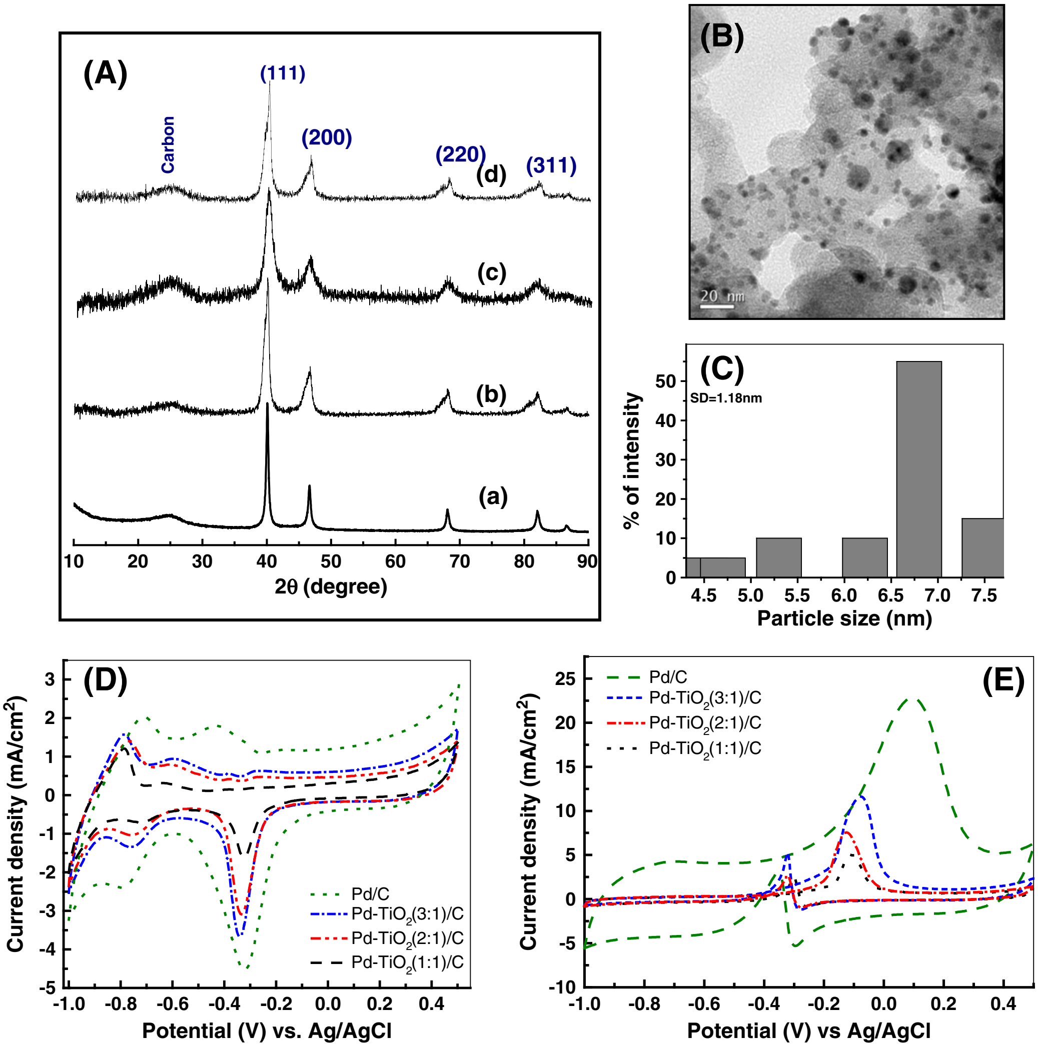

Fig. 1. (A) XRD patterns of (a) Pd/C (b) Pd–TiO_2(3:1)/C (c) Pd–TiO_2 (2:1)/C and (d) Pd–TiO_2 (1:1)/C, (B) TEM image for Pd–TiO_2 (3:1)/C and (C) corresponding histogram, (D) CV of Pd/C and Pd–TiO_2/C in 0.1 M KOH and (E) in aqueous 0.1 M KOH solution containing 0.1 M Methanol.