



Oxygen reduction reaction catalyzed by platinum nanonetwork prepared by template free one step synthesis for polymer electrolyte membrane fuel cells



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ABSTRACT

The reduction reaction of molecular oxygen (ORR) was investigated using supportless Pt nanonetwork (Pt NN) electrocatalyst in sulfuric acid medium. Pt NN was prepared by template free borohydride reduction. The transmission electron microscope images revealed a network like nano-architecture having an average cluster size of 30 nm. The electrochemical characterization of supportless and Vulcan carbon supported Pt NN (Pt NN/VC) was carried out using rotating disc and ring disc electrodes at various temperatures. Kinetic and thermodynamic parameters were estimated under hydrodynamic conditions and compared with Pt NN/VC and reported Pt/C catalysts. The accelerated durability test revealed that supportless Pt NN is quite stable for 5000 potential cycles with 22% reduction in electrochemical surface area (ECSA). While the initial limiting current density has in fact increased by 11.6%, whereas Pt NN/VC suffered nearly 55% loss in ECSA and 13% loss in limiting current density confirming an enhanced stability of supportless Pt NN morphology for ORR compared to conventional Pt/C ORR catalysts in acid medium.

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1. Introduction

The reduction of molecular oxygen in the cathodic part of polymer electrolyte membrane fuel cells (PEMFCs) is a major impediment for the development of fuel cells and their commercialization is still delayed due primarily to the cost of platinum (Pt) catalysts and secondly by the poor stability of the traditional Pt catalysts. Fuel cell catalyst research has witnessed a phenomenal increase in the performance of the Pt and Pt based electrocatalysts in terms of improved utilization, stability and cost reduction [1]. The first generation Pt black catalysts used in space applications as supportless systems possessed the disadvantage of low surface area and under utilization [2]. Later, for improving the electrocatalytic properties and for better surface exposure carbon supported Pt black was used to enhance the mass and specific activities. The most widely used support materials are carbon black, graphene, single and multi walled carbon nanotubes [3,4]. However, the use of carbon support has some undesirable outcomes such as carbon surface corrosion and oxidation to CO₂

leading to loss of both highly expensive Pt content and efficiency due to Ostwald ripening, migration and agglomeration of catalyst nanoparticles [5–7]. Due to the tremendous development in nanotechnology supportless electrocatalysts based on Pt were prepared and reported by many to find the effect of different surface morphologies on catalytic activity as described below.

In many cases, the supportless Pt nanocatalyst systems were found to possess an increased stability than Pt/C catalysts as reported in literature. Chen et al. have synthesized the Pt nanotubes by galvanic replacement reaction and tested their suitability for the oxygen reduction reaction (ORR) in acid medium. They observed nearly 20% reduction in electrochemical surface area (ECSA) after 1000 potential cycles [8]. Sun et al. have synthesized ‘multiarmed star like Pt nanowires’ through formic acid reduction and tested the ORR activity. They observed ca. 12% loss in ECSA after 4000 potential cycles [9]. Pt netlike nano-assembly as highly durable electrocatalyst for ORR reported by Wang et al. demonstrated that polyvinyl pyrrolidone (PVP) and sodium lauryl sulphate stabilized reduction of K₂PtCl₆ using sodium citrate yielded ‘network like nanoparticles’ with the improved stability. After 20,000 cycles nearly 9% ECSA has decreased but there is no mention about the trend in limiting current during potential cycling to understand about the kinetics

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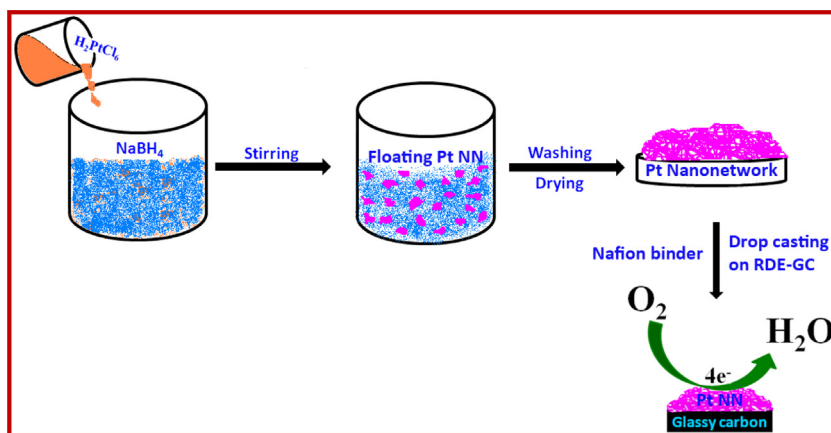


Fig. 1. Schematic representation of synthesis of supportless Pt nanonetwork.

of ORR [10]. CTAB and oleyamine assisted synthesis of Pt nanoassemblies for ORR has been reported by Xia et al. They noted nearly 27% loss in ECSA after 10,000 potential cycles [11] and nearly 17% limiting current has reduced after 3000 potential cycles. Xu et al. have synthesized 3D Pt nanochain networks and investigated the electrochemical activity for ORR. They noticed a loss of ca. 14.4% ECSA after 1000 potential cycles [12]. Lee et al. have reported the synthesis of mesoporous Pt nanosponge by PVP assisted galvanic displacement method and found the size dependent electrocatalytic activity towards ORR [13]. Most of the above synthesis methods use either a template or multistep or non-scalable processes, and usually yield Pt nanostructures with low surface area. Since the synthesis method and structural morphology greatly affect the activity and stability of Pt catalyst systems, investigating the effect of Pt nanostructure on stability is still a focused area of recent research and finding a compromised optimum between the activity and stability is still underway.

Here, we report a template free synthesis of Pt nanonetwork by simple reduction process and investigate the catalytic activity for oxygen reduction reaction in acid medium. The obtained Pt NN was surface characterized using X-ray diffraction (XRD), high resolution transmission electron microscope (HR-TEM) and electrochemically characterized towards ORR in sulfuric acid electrolyte under hydrodynamic conditions at various temperatures using rotating disc electrode (RDE) and rotating ring disc electrodes

(RRDE). The kinetic parameters were derived and mechanism of ORR was proposed and discussed.

2. Experimental

Chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, Aldrich) was used as the platinum precursor. Sodium borohydride (NaBH_4 , Fluka) was used as reducing agent. Nafion perfluorinated ionomer resin solution (5 wt.%, Aldrich, equivalent weight 1100) dissolved in aliphatic alcohol was used as the binding material. Absolute ethanol (sd fine, India) was used as solvent to prepare the catalyst ink. Vulcan XC-72 carbon (Cabot) was used as the carbon support. High pure nitrogen and oxygen gases (AR grade) were procured from Praxair, India. Sulfuric acid (H_2SO_4 , Rankem, India) was used as the electrolyte. All the materials were used as received. Millipore water ($18\text{ M}\Omega\text{ cm}$) was used for all solution preparations.

Pt NN was synthesized by adopting our earlier reported procedure [14]. In a typical synthesis 10 mL of an aqueous solution of 0.1 M $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ was added to 50 mL of an aqueous solution of freshly prepared 0.1 M NaBH_4 (1:5 v/v ratio of $\text{H}_2\text{PtCl}_6/\text{NaBH}_4$ solution) with stirring. The floating solid was filtered and washed with distilled water and dried at room temperature. For synthesizing 20 wt.% Pt NN/VC, a known amount of carbon was taken along with metal precursor during reduction.

XRD patterns were recorded using Bruker-D8 diffractometer with $\text{Cu-K}\alpha$ radiation, ($\lambda = 1.54\text{ \AA}$, step size: 0.02, current: 30 mA and voltage: 40 kV) and the mean nanoparticle size was calculated using Scherrer equation. The surface morphology of the nanonetwork was examined with high resolution TEM images taken using JEOL JEM-3010 electron microscope with an accelerating voltage of 300 kV.

For an electrochemical investigation, the glassy carbon disc electrode (GC-RDE, Pine) was used. The catalyst ink was prepared by dispersing 0.5 mg of Pt NN in 995 μL of absolute ethanol and 5 μL of 5 wt.% Nafion and ultrasonicated the resulting mixture for 5 min. The surface of GC-RDE was modified with a 5 μL portion of this catalyst ink by drop casting to obtain the metal loading of $12.7\text{ }\mu\text{g cm}^{-2}$ Pt. The same loading was maintained for Vulcan carbon supported Pt NN catalyst. Prior to coating, the GC surface was polished with 0.05 μm alumina slurry washed with ethanol and water and then subjected to ultrasonic surface cleaning for 5 min in deionized water. After thorough drying, the catalyst coated GC electrode was used for electrochemical measurements. A similar procedure was employed for coating Pt NN/VC. The CV curves of these catalysts were recorded in 0.5 M H_2SO_4 solution with nitrogen gas purging at a sweep rate of 100 V s^{-1} using a

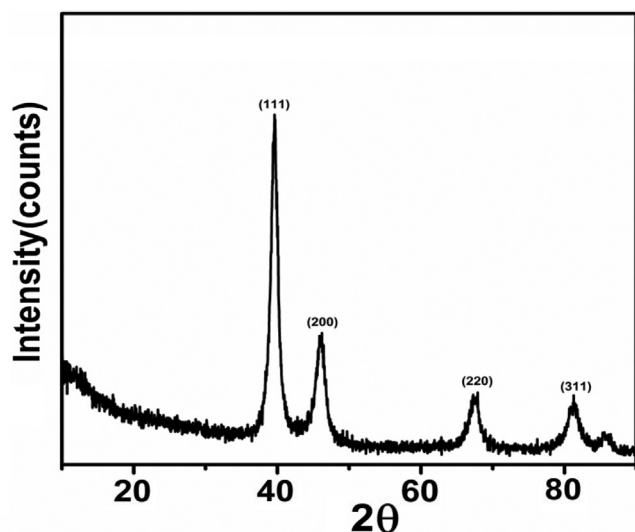


Fig. 2. XRD patterns of supportless Pt nanonetwork.

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