

Metal Oxide/Pt Based Nanocomposites as Electrocatalysts for Oxygen Reduction Reaction

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Abstract

Fuel cell is a promising choice for clean energy because of its eco-friendly system, high energy conversion efficiency and high power density. Recently, much of the research work is focused on the system of combining metal oxides to increase the durability and surface area and to reduce the cost. In this study, among the various fabrication methods, we used the precipitation method to synthesis composites Pt/C/SnO₂/NiO using NaBH₄ as a reducing agent. XRD and SEM characterizations were carried out to determine the particle size and distribution of the catalysts. Cyclic voltammetry were recorded to evaluate Oxygen Reduction Reaction (ORR). SEM images revealed that Pt/C and metal oxide nanoparticles were uniformly dispersed in the composite catalyst architecture with smaller particle size for composite/Pt/C catalyst compared to Pt/C catalysts. XRD patterns of samples showed peaks characteristic of metal Pt and of rutile and cubic phases for SnO₂ and NiO, respectively. The onset potentials for ORR on Pt/C and Pt/C/SnO₂/NiO catalysts are 0.28 and 0.21 V, respectively, confirming that later has higher activities than Pt/C. The onset potential for oxygen reduction is shifted to more positive potential for binary metal oxides modified compared to Pt/C.

Key words: Fuel Cell, Metal Oxide, Precipitation Method, Oxygen Reduction Reaction

Highlights

- Composite support combining carbon and metal oxides to develop more durable ORR catalysts for cathodic performance in PEM fuel cell applications.
- Improved ORR due to the ready adsorption and easy dissociation of O₂ on the metal oxide modified Pt surface.
- More positive potential shift for binary metal oxides NiO-SnO₂ modified Pt surface in relation to Pt/C.

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Introduction

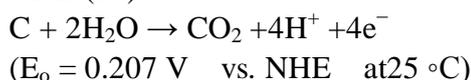
Proton exchange membrane fuel cells (PEMFCs) have received considerable attention in recent years as alternative energy devices for transportation and portable power generation applications (1). However, two main challenges limit the application of fuel cells in transport (2): (i) the sluggish kinetics of the Oxygen Reduction Reaction (ORR) on the cathode side due to the formation of $-OH$ species at +0.8 V, which inhibits further reduction of oxygen and hence, results in loss of performance (3) and then, more active catalysts should be used (4); and (ii) the high cost of the whole device limits their commercialization (5). However, the highest electrocatalytic activity is still gained at Pt and Pt-based alloys.

It has been shown that several factors can diminish the lifetime of PEMFCs including (1) catalyst dissolution, (2) catalyst particle sintering, (3) membrane thinning, and (4) carbon-support corrosion (6, 7).

The cathode performance improvement could be achieved using supported Pt catalysts of higher surface area and lower platinum loading including Pt-based alloys with transition metals such as Sn (8) and Ni (9). Tin oxide (SnO_2), with n-type semiconducting property, high electronic conductivity, and good Electrochemical stability, has been proposed as a potential catalyst support material for fuel cell application (10, 11). In addition, NiO showed an excellent Electrochemical performance as an electrode material for lithium ion batteries and fuel cells (12). These properties recommend consideration of NiO as an alternative catalyst support. However, its low electrical conductivity prevents its use in fuel cells. Carbon (e.g.,

Vulcan XC-72) is the typical catalyst support material for PEM-based fuel cells due to its large surface area, high electrical conductivity, and well-developed pore structure (13).

The potential of the cathode can reach as high as 1.5 V, causing severe carbon corrosion as indicated by the following reaction (14):



The Electrochemical corrosion of the carbon support causes: (i) agglomeration and sintering of the Pt catalyst particles, resulting in a decreased Electrochemical surface area of the catalyst; (ii) electrically isolated Pt particles that are detached from the support. These effects result in a rapid degradation of the Pt catalyst and thus shorten the lifetime of the PEMFC. Therefore, more robust non-carbon support materials, such as metal oxides, are needed. Metal-metal oxide catalysts have been investigated as possible co-catalysts that are believed to operate via the bifunctional mechanism (15).

In this study, Pt catalyst was precipitated on Vulcan XC-72R containing 10 wt. % NiO and SnO_2 using $NaBH_4$ as a reducing agent. XRD and SEM characterizations were carried out to determine the particle size and distribution of the catalysts. Cyclic voltammetry and linear sweep voltammetry were recorded to evaluate Oxygen Reduction Reaction (ORR) performance.

There is not such a study, to the best of our knowledge, with the composite support combining carbon and metal oxides to develop more durable ORR catalysts for cathodic performance in PEM fuel cell applications.

Experimental

Reagents: $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{K}_2(\text{Pt}(\text{OH})_6)$ was used as Sn, Ni and Pt precursor, respectively. Vulcan XC-72R carbon black was purchased from Cabot Corp., USA with a specific surface area (BET) of $240 \text{ m}^2 \text{ g}^{-1}$ and an average particle size of 40 nm. Ethanol, NaBH_4 , isopropanol, citric acid, NaOH, and H_2SO_4 were obtained from Sigma–Aldrich, Germany. Nafion (perfluorosulphonic acid–PTFE copolymer, 5 wt.% solution), ethylene glycol and 1,2-dimethoxyethane were purchased from Fluka. All chemicals were used as received without further purification. De-ionized water was used to prepare the solutions.

Pt– $\text{SnO}_2/\text{NiO}/\text{C}$ electrocatalysts preparation: Preparation of Pt/C/ SnO_2/NiO electrocatalysts: Supporting NiO and SnO_2 on Vulcan XC-72R carbon black by the precipitation method, followed by the chemical reduction of Pt precursor salt using NaBH_4 as the reducing agent. The detailed steps of the catalyst manufacture were as follows: an appropriate amount of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (10 wt.%) was weighed and dissolved in a suspension of Vulcan XC-72R carbon black in double distilled water. Drops of 1 M NaOH solution were added to the mixture to maintain its pH value at 10 during the constant stirring for 3 h. This induces the formation of small and uniform nanoparticles. The resulting powder was then filtered and washed with double distilled, dried at $80 \text{ }^\circ\text{C}$. Calcination step at $600 \text{ }^\circ\text{C}$ was performed in air muffle for 3 h to form $\text{SnO}_2/\text{NiO}/\text{C}$ catalyst. The corresponding volume of $\text{KPt}(\text{OH})_6$ (Pt loading 10 wt.%) was added in a

suspension of NiO/C powder in double distilled water, sonicated and the reduction step was performed by adding NaBH_4 solution slowly with continuous stirring for 3 h. The formed Pt/C/ SnO_2/NiO catalyst was then filtered and washed, and drying step was performed in an air oven at $80 \text{ }^\circ\text{C}$ for 6 h.

The electrocatalyst ink was prepared by ultrasonating 10 mg of electrocatalyst in 500 ml of ethanol followed by adding 25 ml of Nafion (5 wt%) and ultasonicated further. 2 ml of the ink was drop casted over glassy carbon electrode using micropipette. The electrode was dried in ambient condition.

For material characterization, The X-ray powder diffraction (XRD) pattern of material was collected on a Bruker, D8 ADVANCE XRD diffraction spectrometer with a Cu $\text{K}\alpha$ line at 1.5406 Å and a Ni filter for an angle range of $2\theta = 10\text{--}90^\circ$ for the determination of crystal structure of composite support as well as their supported catalysts. The morphology of the materials was observed on a Philips, XL30 scanning electron microscope (SEM) with an accelerating voltage of 17 kV.

Electrochemical measurements of the electrocatalysts: Cyclic voltammeteries were recorded to evaluate ORR performance. Cyclic voltammograms were obtained in a conventional three electrode Electrochemical cell. The working electrode used for Electrochemical measurement was glassy carbon electrode of diameter 3mm with a thin layer of electrocatalyst ink drop casted over it. A Pt electrode used as the counter electrode and an Ag/AgCl electrode saturated with 1 M KCl was used as the reference electrode.

Results and Discussion

Structural characterization: Fig. 1 shows the XRD patterns of synthesized Pt/SnO₂/NiO catalyst. The SnO₂ peaks at can be respectively indexed to the (1 1 0), (1 0 1), (2 0 0), and (2 1 1) reflections of cassiterite SnO₂ (JCPDS no. 41-1445). NiO with a cubic structure (bunsenite, NaCl type structure) was observed ((JCPDS no. 44-1159). The presence of metallic Pt is also clearly revealed by the peak at 39.9° and 46.2° attributed to the Pt (1 1 1) and (2 0 0) reflection, respectively (JCPDS no. 1-1311)

(16). The broadening of two peaks indicates the small particle size of Pt.

Morphological analysis: As shown in Fig. 2, SnO₂ and NiO nanoparticles are uniformly dispersed on the surface Pt/C support. SEM images revealed that Pt/C and metal oxide nanoparticles were uniformly dispersed in the composite catalyst architecture with smaller particle size for composite/Pt/C catalyst compared to C catalysts.

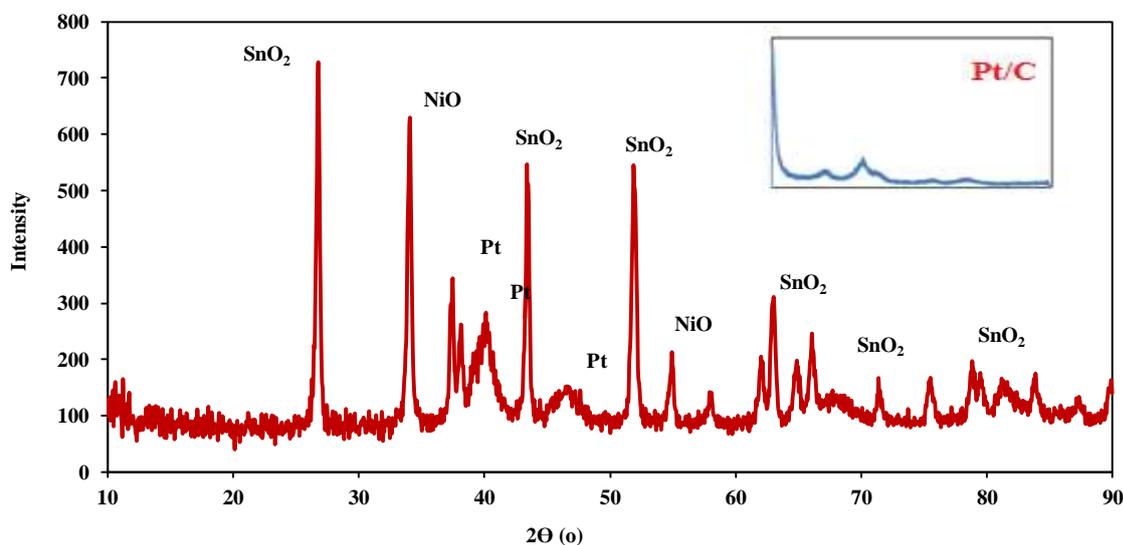


Fig. 1- XRD pattern of Pt/C and Pt–NiO/SnO₂ electrocatalysts.

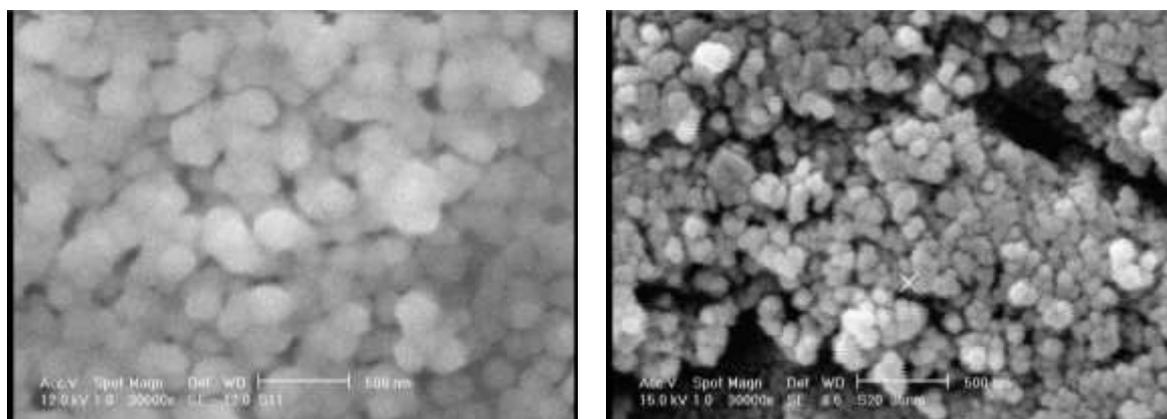


Fig. 2- SEM images of Pt/C (left) and Pt–NiO/SnO₂ electrocatalysts (right).

Electrochemical measurements results: Cyclic voltammetric technique has been proven to be very useful in obtaining information on the stability in the reaction media and participation of the active sites on the electrode surfaces. The cyclic voltammograms of both Pt/C and Pt/C/SnO₂/NiO are presented in Fig. 3. Cyclic voltammograms of typical Pt features are obtained, with H₂ adsorption/desorption regions and Pt oxidation/reduction peaks. The onset

potentials for ORR on Pt/C and Pt/C/SnO₂/NiO catalysts are 0.28 and 0.21 V, respectively confirming that later has higher activities than Pt/C. The onset potential for oxygen reduction is shifted to more positive potential for binary metal oxides modified compared to Pt/C. The improved ORR is due to the ready adsorption and easy dissociation of O₂ on the NiO-SnO₂ modified Pt surface in relation to Pt/C.

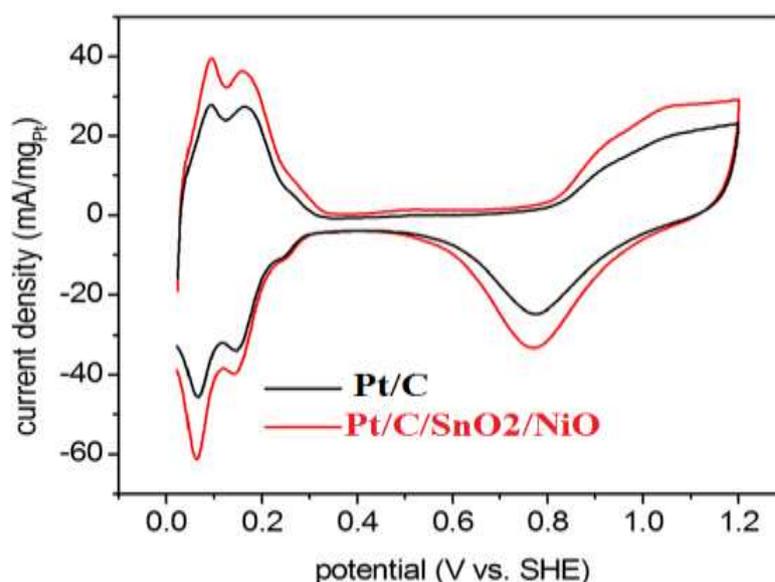


Fig. 3- Cyclic voltammograms of Pt/C and Pt/C/SnO₂/NiO electrodes in 0.5 M H₂SO₄.

Previous reports showed that a shift to the higher potential values for Pt oxide/reduction peak is associated with an enhanced in the Pt catalytic activity for reduction reactions (ORR) (17).

In addition, the strong interaction between metal catalyst Pt and metal oxide support such as SnO₂ (18) and NiO (19) and bifunctional synergistic effects simultaneous presence of metal oxides as a second catalyst (co-catalyst) may also be responsible for the enhanced activity (20).

In the past several years, the lithiated NiO had been extensively used and exhibited excellent fuel cell performance as cathode. The lithiated NiO have also been demonstrated to show the potentiality for oxygen reduction in low temperature FC (21).

As a cocatalyst, SnO₂ was also found to enhance the activity of Au toward ORR, the activity of Pt over MOR, ethanol oxidation because of its high electronic conductivity, and stability in low temperature fuel cell working conditions (22, 23).

These results show that the metal oxide support can affect the activity and stability of the cathode in the polymer electrolyte fuel cell. An enhanced activity was observed for ORR. This could indicate that the platinum surface is less covered by oxides, a hypothesis supported by the postponed oxide formation seen in the cyclic voltammograms of platinum deposited. However, the reason for the improved activity for ORR on the nickel oxide electrodes are not fully understood.

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