



Synthesis and Characterization of Ruthenium-Titanium Composite Oxide and a Platinum Catalyst Supported on It

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Abstract: Ru_{0.1}Ti_{0.9}O₂ nanopowder was synthesized from TiN nanoparticles and RuCl₃ precursors by the impregnation-thermal decomposition method. A supported Pt/Ru_{0.1}Ti_{0.9}O₂ electrocatalyst was prepared using this as the support by solid phase synthesis. X-ray diffraction and transmission electron microscopy results indicate that RuO₂ and TiO₂ formed a binary solid solution with rutile phase. Pt nanoparticles were deposited uniformly on the surface of the solid solution. Pt/Ru_{0.1}Ti_{0.9}O₂ showed good electrocatalytic properties as characterized by hydrogen and oxygen evolution in the polarization curves measured in 0.5 mol/L H₂SO₄. This was due to a synergistic effect between Pt and Ru_{0.1}Ti_{0.9}O₂. Pt/Ru_{0.1}Ti_{0.9}O₂ also showed high electrocatalytic activity in oxygen reduction as a proton exchange membrane fuel cell cathodic catalyst. Pt/Ru_{0.1}Ti_{0.9}O₂ showed much better stability than Pt/C in an anti-polarization experiment.

Key words: titanium nitride; ruthenium oxide; titania; impregnation-thermal decomposition; fuel cell; water electrolysis; catalyst support; conductive oxide

Supported catalysts, esp. carbon supported platinum (Pt/C), have been used in the past few years in proton exchange membrane fuel cells (PEMFCs) because these can decrease the amount of noble metals used [1]. However, corrosion of the carbon supports was observed under PEMFC operating conditions [2,3]. This has led to the loss of activity in the cell [4], esp. at high temperatures (120–200 °C) [5]. Also, carbon cannot be used as the support in catalysts for PEM-water electrolysis and regenerative fuel cells because its corrosion occurs easily at the high oxygen-evolution potential [6,7]. Some new catalyst supports for these applications are electric ceramic powders (TiC, TiN, WC, WO₃, and TaC) [8], ITO (indium and stannum oxide) [9], titanium oxide (Ebonex and Ti₄O₇) [10], and Nb-TiO₂ [11]. Thus, the synthesis of the electric ceramic or oxide as a nanoscale powder with high conductivity is being investigated.

As an electrical metal oxide, the dimension stable anode (DSA) is used as a coating mixed with noble metal (as the

active element) and metal oxides. It has the advantages of high conductivity, catalytic activity and stability, and low noble metal content [12]. The Ru_xTi_{1-x}O₂ prepared by Haas et al. [13] using a sol-gel process had the disadvantage of too large a particle size of ca. 200–300 nm that did not have good conductivity until a high Ru content (> 27 mol%). The Pt/IrO₂, prepared and used in a regenerative fuel cell by Yao et al. [14] showed excellent electrocatalytic performance but had a large amount of noble metal. We have reported the solid phase synthesis from TiN by an impregnation-thermal decomposition method [15] operated in the mid-to-low temperature range. This has the characteristics of a simple technology, high purity product, no waste water and can be industrialized. In this study, a Ru_{0.1}Ti_{0.9}O₂ nanopowder was synthesized and used as the support to give Pt/Ru_{0.1}Ti_{0.9}O₂. Its electrocatalytic performance using hydrogen and oxygen evolution in water electrolysis and oxygen reduction in a PEMFC was investigated.

The Ru_{0.1}Ti_{0.9}O₂ (10 mol% Ru) nanopowder was synthesized

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by the impregnation-thermal decomposition method from TiN nano-particles (99%, 20 nm, from HFKILN China) and a RuCl_3 precursor (37 wt% Ru, from PGMCHINA) [15]. $\text{Pt/Ru}_{0.1}\text{Ti}_{0.9}\text{O}_2$ (20 wt% Pt) was prepared by the solid phase synthesis method [16] from $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (38 wt% Pt, from PGM CHINA) and $\text{Ru}_{0.1}\text{Ti}_{0.9}\text{O}_2$. In order to study the interaction between Pt and the support, platinum black (Johnson Matthey) and $\text{Ru}_{0.1}\text{Ti}_{0.9}\text{O}_2$ were mechanically mixed to give $\text{Pt-Ru}_{0.1}\text{Ti}_{0.9}\text{O}_2$ (20 wt% Pt). The composition, size and morphology of $\text{Ru}_{0.1}\text{Ti}_{0.9}\text{O}_2$ and $\text{Pt/Ru}_{0.1}\text{Ti}_{0.9}\text{O}_2$ were characterized by XRD (D8 Advance, Germany) and TEM (JEOL JEM-2010, Japan).

The working electrode in a H_2SO_4 solution was prepared following Sun et al. [15]. The content of the supported powder catalyst on the nonporous graphite plate was about 1.0 mg/cm^2 . The preparation of the PEMFC membrane electrode also followed Sun et al. [15]. The surface area of the working electrode was 6.25 cm^2 . The Pt content was 0.4 mg/cm^2 in the cathode and anode. The polarization curves were measured at room temperature using a Princeton Applied Research (PAR 273A) potentiostat/galvanostat at a sweep rate of 1 mV/s . A conventional three-electrode cell was used with platinum sheet as a counter electrode. A saturated calomel electrode (SCE) was the reference electrode. The solution resistance was measured by the electrochemical impedance spectrum (EIS) at the corrosion potential. The polarization curves were corrected by subtracting the solution voltage. The PEMFC was a PhyX single cell (Shanghai Pearl Hydrogen Power Source Technology Co. Ltd) at 60°C , atmosphere pressure, and no humidification.

In order to compare the stability of $\text{Pt/Ru}_{0.1}\text{Ti}_{0.9}\text{O}_2$ with Pt/C easily and quickly, the anti-polarization experiment was performed after shutdown of the PEMFC. First, the normal ventilation and test conditions of the PEMFC were kept, and the air and hydrogen side electrodes were connected with the positive and negative poles of the DC power supply, respectively. Second, a cell voltage of 2.0 V was applied for 20 min and then stopped to operate on the PEMFC again, and the current density was measured at 0.7 V .

Fig. 1 shows the XRD patterns of $\text{Ru}_{0.1}\text{Ti}_{0.9}\text{O}_2$ and $\text{Pt/Ru}_{0.1}\text{Ti}_{0.9}\text{O}_2$. From the shape and location of the peak in Fig. 1(1), we can deduce that the $\text{Ru}_{0.1}\text{Ti}_{0.9}\text{O}_2$ nanopowder has better crystallinity and nearly the same peak positions as rutile TiO_2 . There was no diffraction peak of Ru or RuO_2 . Because Ru^{4+} and Ti^{4+} have similar ion radii and RuO_2 and TiO_2 exist in the same rutile crystal structure, the substitution between RuO_2 and TiO_2 is very easy, and $\text{Ru}_{0.1}\text{Ti}_{0.9}\text{O}_2$ can exist as a solid solution. This is consistent with the DSA results [17]. The crystal particle size of $\text{Ru}_{0.1}\text{Ti}_{0.9}\text{O}_2$ calculated by the Scherrer formula was about 14 nm . The Pt diffraction peaks in the XRD spectrum (Fig. 1(2)) were broadened, and their positions were shifted to the left. This indicated a possible strong interaction between the support $\text{Ru}_{0.1}\text{Ti}_{0.9}\text{O}_2$ and deposited Pt particles, which has been discussed by Krstajic et al. [18].

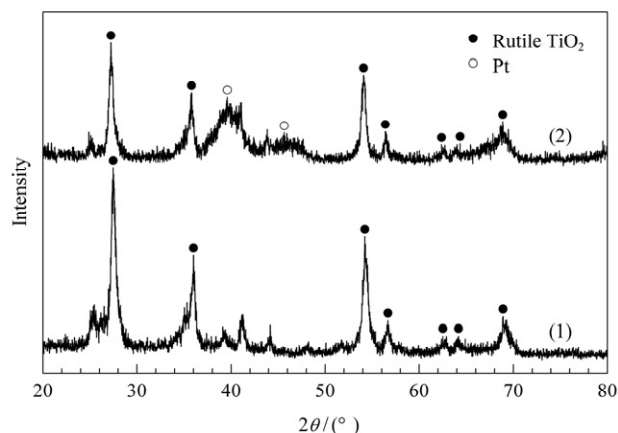


Fig. 1. XRD patterns of $\text{Ru}_{0.1}\text{Ti}_{0.9}\text{O}_2$ (1) and $\text{Pt/Ru}_{0.1}\text{Ti}_{0.9}\text{O}_2$ (2).

The TEM micrographs of $\text{Ru}_{0.1}\text{Ti}_{0.9}\text{O}_2$ and $\text{Pt/Ru}_{0.1}\text{Ti}_{0.9}\text{O}_2$ are shown in Fig. 2. Fig. 2(a) shows that the $\text{Ru}_{0.1}\text{Ti}_{0.9}\text{O}_2$ nanopowder comprised well-dispersed single rods with a small amount of agglomerates. The radial sizes were similar to the average crystal particle size found from XRD. The lengths were longer, which indicated the preferential growth of the crystals along the length. Fig. 2(b) shows that the ultrafine Pt particles were dispersed uniformly on the surface of the $\text{Ru}_{0.1}\text{Ti}_{0.9}\text{O}_2$ rods. The characteristics of the $\text{Ru}_{0.1}\text{Ti}_{0.9}\text{O}_2$ nanopowder did not change after Pt deposition.

The polarization curves for hydrogen evolution and oxygen evolution from mixed $\text{Pt-Ru}_{0.1}\text{Ti}_{0.9}\text{O}_2$ and supported $\text{Pt/Ru}_{0.1}\text{Ti}_{0.9}\text{O}_2$ are showed in Fig. 3. It can be seen that both exhibited excellent hydrogen evolution activity, but there was a large difference in oxygen evolution activity. Due to the weak oxygen evolution catalytic activity of Pt [19], it is natural that there was no improvement in oxygen evolution catalytic activity by simple mechanical mixing. On the other hand, $\text{Pt/Ru}_{0.1}\text{Ti}_{0.9}\text{O}_2$ showed good oxygen evolution catalytic activity. This was attributed to the synergetic effect between Pt and $\text{Ru}_{0.1}\text{Ti}_{0.9}\text{O}_2$ mentioned above.

The comparison of the performance of $\text{Pt/RuO}_2\text{-TiO}_2$ with a commercial Pt/C made by E-TEK indicated that both had similarly good electrocatalytic activity as a cathodic catalyst in the PEMFC at 60°C , atmospheric pressure, and no humidifi-

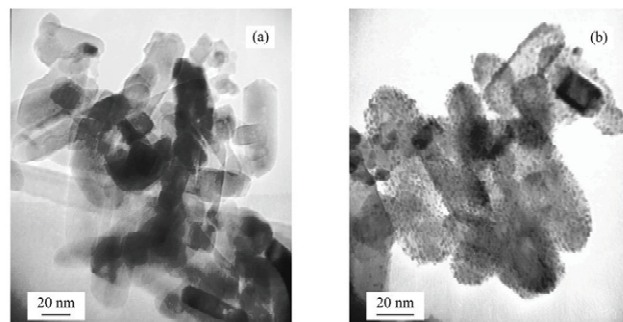


Fig. 2. TEM images of $\text{Ru}_{0.1}\text{Ti}_{0.9}\text{O}_2$ (a) and $\text{Pt/Ru}_{0.1}\text{Ti}_{0.9}\text{O}_2$ (b).

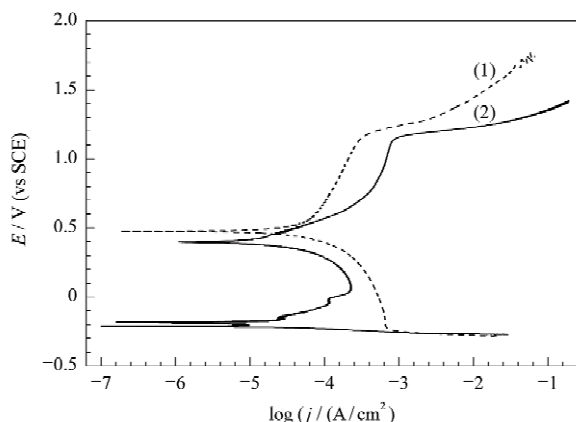


Fig. 3. Polarization curves of Pt-Ru_{0.1}Ti_{0.9}O₂ (1) and Pt/Ru_{0.1}Ti_{0.9}O₂ (2) in 0.5 mol/L H₂SO₄ solution.

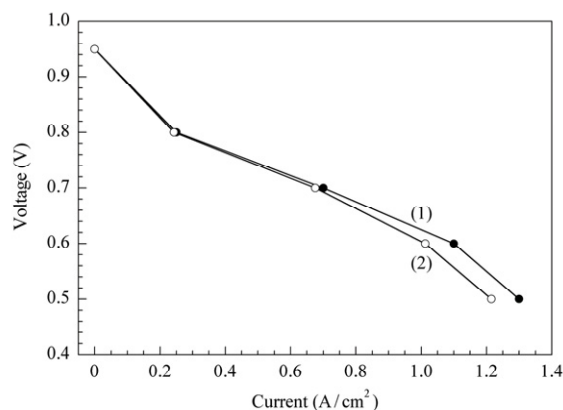


Fig. 4. Voltage-current curves of PEMFC with different cathodic catalysts. (1) Pt/C (E-TEK); (2) Pt/RuO₂-TiO₂.

cation (see Fig. 4). After the anti-polarization experiment, the PEMFC performance of Pt/C as a cathode electrocatalyst decreased from 700 to 150 mA/cm² (at 0.7 V). In contrast, there was no change in the electrocatalytic activity with Pt/RuO₂-TiO₂. Because the membrane electrode prepared here was similar to that using Pt/C, by considering the huge difference in hydrophilicity, volume, and density between Pt/C and Pt/RuO₂-TiO₂, it is expected that a higher PEMFC electrocatalytic activity can be obtained by modifying the preparation techno-

logy of the membrane electrode to give Pt/RuO₂-TiO₂ characteristics.

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