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Magnéli TiO₂ as a High Durability Support for the Proton Exchange Membrane (PEM) Fuel Cell Catalysts

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Abstract: Proton exchange membrane fuel cells (PEMFCs) cathode catalysts' robustness is one of the primary factors determining its long-term performance and durability. This work presented a new class of corrosion-resistant catalyst, Magnéli TiO₂ supported Pt (Pt/Ti₉O₁₇) composite, synthesized. The durability of a Pt/Ti₉O₁₇ cathode under the PEMFC operating protocol was evaluated and compared with the state-of-the-art Pt/C catalyst. Like Pt/C, Pt/Ti₉O₁₇ exhibited exclusively 4e[−] oxygen reduction reaction (ORR) in the acidic solution. The accelerated stress tests (AST) were performed using Pt/Ti₉O₁₇ and Pt/C catalysts in an O₂-saturated 0.5 M H₂SO₄ solution using the potential-steps cycling experiments from 0.95 V to 0.6 V for 12,000 cycles. The results indicated that the electrochemical surface area (ECSA) of the Pt/Ti₉O₁₇ is significantly more stable than that of the state-of-the-art Pt/C, and the ECSA loss after 12,000 potential cycles is only 10 ± 2% for Pt/Ti₉O₁₇ composite versus 50 ± 5% for Pt/C. Furthermore, the current density and onset potential at the ORR polarization curve at Pt/C were significantly affected by the AST test. In contrast, the same remained almost constant at the modified electrode, Pt/Ti₉O₁₇. This demonstrated the excellent stability of Pt nanoparticles supported on Ti₉O₁₇.

Keywords: catalyst support; catalyst stability; Magnéli; TiO₂; Ti₉O₁₇; ORR; PEM fuel cell; automotive fuel cell; high durability; high stability; corrosion resistance



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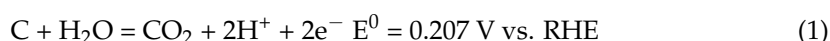
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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) have drawn much attention as a promising energy conversion technology due to their higher conversion efficiency, higher power density, higher current density, and quick startup [1,2]. Among PEMFCs, the high-temperature fuel cell is considered a next-generation technology as it has several advantages at an operating temperature of more than 90 °C [3,4]. There are several advantages to operating at a higher temperature: (i) promoting faster reaction kinetics, especially for the four-electron reduction process at the cathode; (ii) better contamination tolerance; (iii) efficient water control; and (iv) easier straightforward injection. Unfortunately, the catalyst durability is a critical challenge that must be addressed for PEMFC's widespread commercialization since it directly reflects the life and cost of PEMFC's power-generation systems [5]. Carbon black has been the commonly used catalyst support material due to its low cost, high surface area, and availability [6–8]. Although catalyst degradation could result from many factors, the primary contributors are believed to be (i) the dissolution and re-deposition (Ostwald ripening) of Pt, (ii) coalescence via crystal migration, and (iii) detachment of Pt particles from the catalyst support [9]. Among these, Pt detachment results through catalyst support corrosion. Conventional carbon blacks, such as Vulcan XC72R, are superior catalyst-support materials because of their cost and physicochemical properties. However, carbon is unstable under the cathodic operation in a PEMFC based on its thermodynamic considerations.



In order to resolve the issue of carbon support corrosion, several extensive studies have been conducted on adopting materials with high corrosion resistance, including carbon, with a greater degree of graphitization. Several other types of carbon-based materials have been studied, including nanofiber, nanotube, nano-diamond, graphene, and mesoporous structure [10–18]. Although carbon with a higher graphitization degree has higher corrosion resistance versus carbon black, it is still inadequate to mitigate its corrosion under long-term operation due to its intrinsic carbon composition. Therefore, to improve PEMFCs catalyst support stability, considerable work has been done over the past few decades on non-carbon support materials [19–24], including oxides, carbides, and nitrides. However, the improvements are insufficient to prevent performance loss under highly oxidative conditions during automotive start-stop cycles. Among the non-carbon support materials, the following basic criteria should be considered for the improvement of fuel cell activity and durability that includes the high surface area, high corrosion resistance in extreme operating conditions, like under dry or humid environments, a higher resistance in acidic or alkaline media, high conductivity and excellent electrochemical stability [25,26]. The strong physiochemical interaction of supporting materials with the element is highly desirable to improve catalytic activity and stability.

In this work, we have focused on sub-stoichiometric titanium oxide ($\text{Ti}_n\text{O}_{2n-1}$), which is a Magnéli phase of TiO_2 (M- TiO_2), to improve the durability of requirements of the automotive application. The electron conductivity of MTiO_2 obtained by thermally treating TiO_2 in a reducing environment is similar to that of activated carbon [27]. Moreover, chemically inert M- TiO_2 materials have remarkably high electrical conductivity and corrosion resistance [27]. These excellent properties of M- TiO_2 translate it as an excellent candidate for catalyst support for Pt-based catalysts in the PEMFCs [27].

In this study, Ti_9O_{17} was synthesized as M- TiO_2 and then used as catalyst support for Pt catalyst. The activity of oxygen reduction reaction (ORR) of synthesized catalyst was evaluated using O_2 -saturated 0.5 M H_2SO_4 solution, and the stability was evaluated using AST protocol via stop-start cycle over 12,000 cycles. The catalyst support needs to demonstrate <30% degradation to be eligible to use in automotive applications. Ti_9O_{17} support Pt showed excellent activity and stability towards ORR. The ORR activity and stability of the synthesized Pt/ Ti_9O_{17} catalyst were compared with the state-of-the-art Pt/C catalyst.

2. Experimental

2.1. Materials

Pt/C catalyst (20% Pt loading) was purchased from the Fuel Cell Store. Titanium (IV) oxide, anatase (99.7% metal basis), and Pt nanoparticle (~30 nm) were procured from Aldrich. The analytical grade purity materials were used in this study without further purification.

2.2. Catalyst Synthesis and Electrode Preparation

2.2.1. Synthesis of Ti_9O_{17}

Ti_9O_{17} as a support material for PEMFC catalyst was synthesized as follows: 0.45 g of anatase TiO_2 was dispersed in 20 mL of ethanol; the solution was stirred for 80 min. Afterward, the solvent was evaporated at 70 °C with continuous stirring. Finally, the material was reduced at 1050 °C in the mixture of 5% H_2 and 95% N_2 for 5 h. The obtained solid was noted as Ti_9O_{17} .

2.2.2. Synthesis of 30% Pt/ Ti_9O_{17}

The Pt/ Ti_9O_{17} catalyst was prepared as follows: 105.9 mg of Ti_9O_{17} and 45.4 mg of Pt nanoparticle (~30 nm) were mechanically mixed with a pestle and mortar. Then, transferred into a ceramic boat and treated in an inert atmosphere at 400 °C for 3 h. Thus, the obtained solid was noted as Pt/ Ti_9O_{17} catalyst.

2.2.3. Electrode Preparation

Glassy carbon (GC) rotating disk electrodes (RDEs) with 5 mm diameter were used as a working electrode. Before each experiment, the working electrode was polished to a mirror finish with 0.05 μm alumina suspensions and served as an underlying conductive substrate of the working electrode.

Pt /Ti₉O₁₇ (30%) Electrode

10.0 mg Pt/Ti₉O₁₇ catalyst was dispersed ultrasonically in a 1.0 mL mixture of isopropyl alcohol (IPA), water, and 5% Nafion solution (686, 294, and 20 μL , respectively) to prepare the catalyst ink. The dispersion was ultrasonicated for 30 min. A total of 10 μL of the dispersed ink was pipetted out and carefully coated on the top of the RDE. The catalyst layer was dried at room temperature. Thus prepared electrode was dried first at room temperature and then heated in an oven at 130 $^{\circ}\text{C}$ for 30 min in the presence of air. The Pt catalyst loading of the thus prepared electrode was calculated as 0.168 mg/cm^2 .

Pt/C (20%) Electrode

The catalyst ink with Pt/C was prepared in the same way described above. In short, 10.0 mg of Pt/C was dispersed in 1.0 mL of a mixture of the solution, and 15 μL of the dispersion was pipetted out and carefully coated on the top of the GC to get the same amount of Pt loading (0.168 mg/cm^2).

2.3. Surface Characterizations

Powder X-ray powder diffraction (XRD) of the catalyst was performed on an X-ray diffractometer (Smartlab, Rigaku, Tokyo, Japan). The diffractometer was operated at 40 kV and 44 mA using Cu K α radiation at a 4 $^{\circ}$ /min scan rate from 10–80 $^{\circ}$. The energy dispersive X-ray (EDX) spectrometer-assisted field-mission scanning electron microscopy (FEI Quanta 650 FEG SEM) was used for analyzing particle morphology and element composition.

2.4. Electrochemical Measurements

0.5 M H₂SO₄ solution was used as an electrolyte for the electrochemical characterizations with the electrode immersed in the 0.5 M H₂SO₄ solution. Before each electrochemical measurement, the electrolyte solution was purged for 15 min with N₂ gas. The RDE voltammetric measurements were carried out using the PINE Rotating Electrode speed controller in an O₂-saturated solution and recorded at various rotation rates during the ORR study. All currents measured during the experiments were normalized by the geometric surface area of the electrode to current densities.

2.5. Accelerated Stress Test (AST) via Start-Stop Cycles

The stability of the PEMFC catalyst support is usually evaluated through the AST start-stop cycles developed by Nissan. The AST cycle involved a square wave from 0.6 V to 0.95 V with a 3 s dwell time at each potential [28]. The stability of catalysts (Pt/C and Pt/Ti₉O₁₇) is evaluated for 12,000 cycles according to the protocol scheme shown in Figure 1. In the protocol, initial CVs were performed in 0.5 M H₂SO₄ saturated with N₂ gas followed by ORR stability for 12,000 cycles, ORR at O₂-saturated, and finally CVs again in 0.5 M H₂SO₄ solution saturated with N₂ gas.

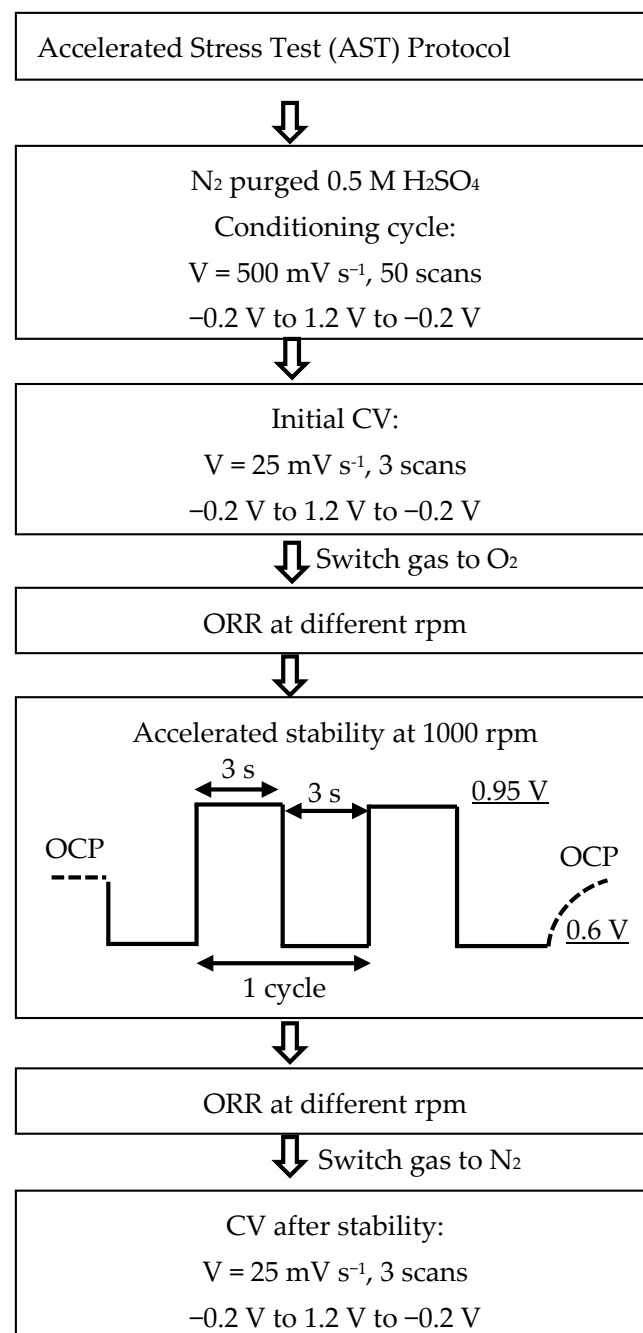


Figure 1. AST protocol scheme for PEM fuel cell catalyst evaluation.

3. Results and Discussion

Figure 2a illustrates the XRD patterns of the Ti₉O₁₇ with standard reference spectra of Ti₉O₁₇. The Magnéli titania phases found in the XRD analysis were mainly Ti₉O₁₇ [29,30]. The synthesized Ti₉O₁₇ was found to be crystalline, and the crystallite size was calculated using the Scherrer equation from the XRD diffraction peak width [31]:

$$L = \frac{K\lambda}{\beta \cos \theta} \quad (2)$$

where L is the particle size, K is a constant, normally taken as 0.9; λ is the X-ray wavelength in nanometer (0.15418 nm) and β is the peak width of the diffraction peak profile at half maximum height in radians. The crystallite size was calculated as 31 nm.

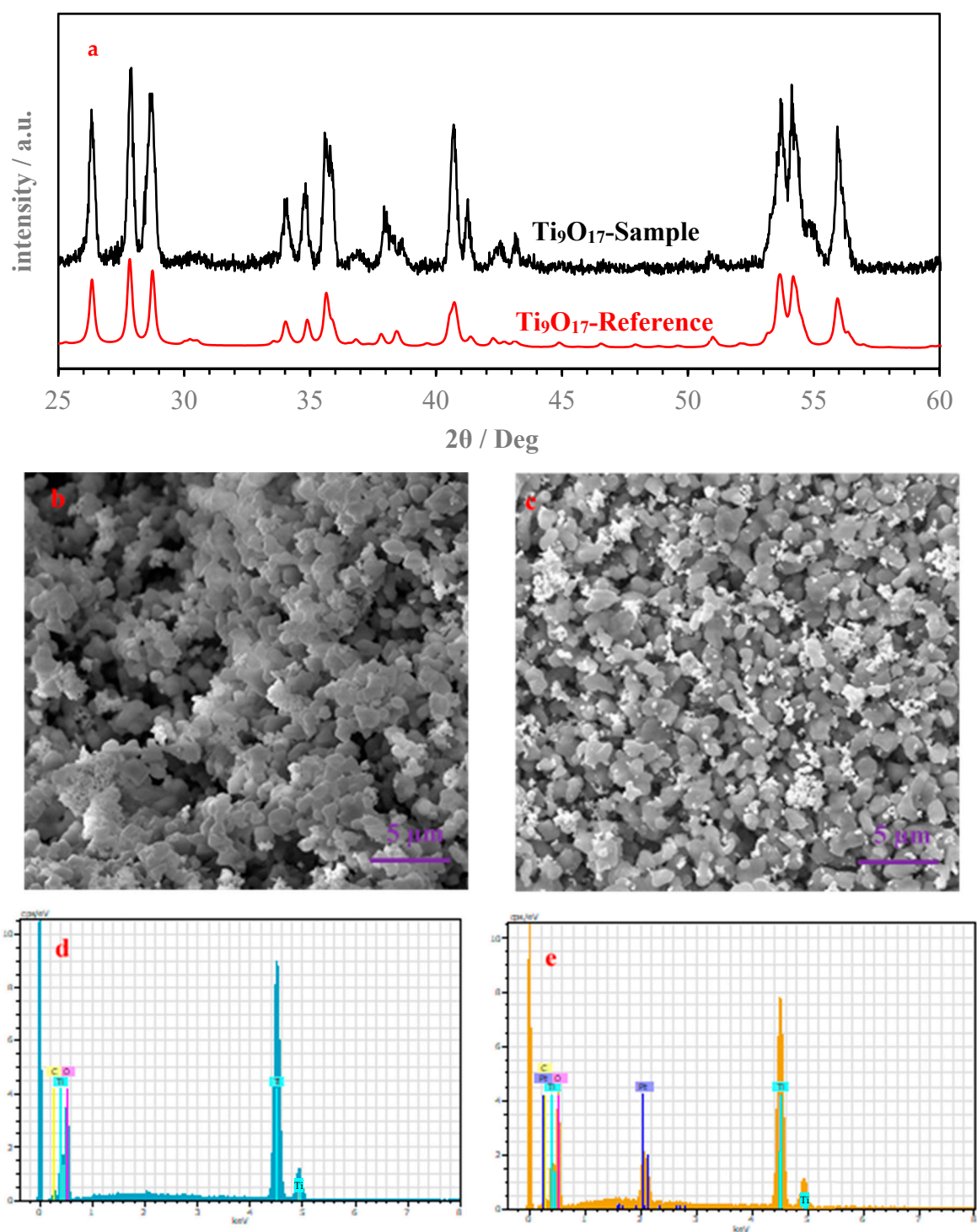


Figure 2. (a) XRD spectra of Ti₉O₁₇ along with a reference (ICSD # 035124) spectrum. SEM images of (b) Ti₉O₁₇ and (c) Pt/Ti₉O₁₇. EDS spectra of (d) Ti₉O₁₇ and (e) Pt/Ti₉O₁₇.

Figure 2b,c shows the SEM images of Ti₉O₁₇ and Pt/Ti₉O₁₇, respectively. As seen from these figures, there is no significant difference in the morphology and distribution of Ti₉O₁₇ and Pt/Ti₉O₁₇. The Pt nanoparticles are evenly distributed on the Ti₉O₁₇ surface.

The EDX pattern of the Ti₉O₁₇ and Pt/Ti₉O₁₇ electrocatalyst (Figure 2d,e, respectively) clearly shows an elemental characteristic of the catalyst surface, that is, the presence of Ti, O, C in the Ti₉O₁₇ sample and Pt, Ti, O, C in the Pt/Ti₉O₁₇ sample.

Electrochemical surface-active area (ECSA). Figure 3 shows the cyclic voltammogram (CV) obtained for the state-of-the-art Pt/C catalysts and experimental Pt/Ti₉O₁₇ catalyst in an N₂-saturated 0.5 M H₂SO₄ electrolyte solution.

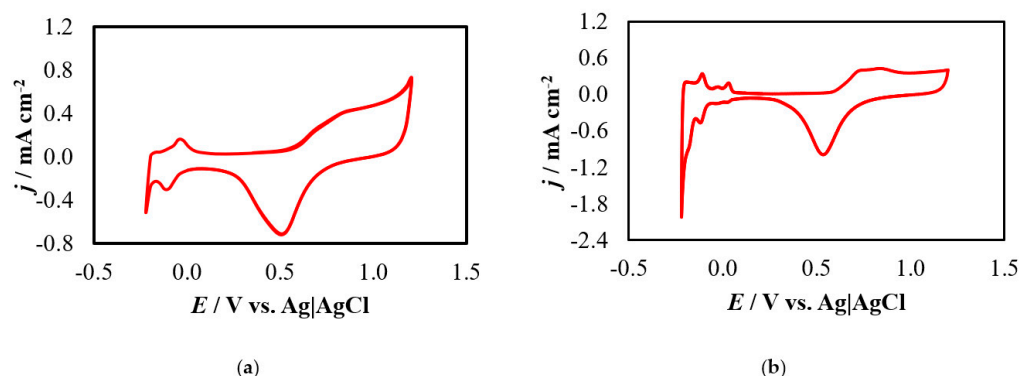


Figure 3. Cyclic voltammogram (CV) obtained using the rotating disk electrodes with (a) state-of-the-art Pt/C catalyst and (b) Pt/Ti₉O₁₇ catalyst in N₂-saturated 0.5 M H₂SO₄ solution at a scan rate of 25 mV s^{−1}.

A characteristic CV response expected for the Pt electrode is obtained for both the Pt/C and Pt/Ti₉O₁₇ electrocatalysts (Figure 3) corresponding to the hydrogen adsorption-desorption and the oxide layer formation and its reduction. The ECSA is calculated from the coulombic charges measured during the hydrogen oxidation step after correcting for double layer charging current using the following equation:

$$\text{ECSA} = \frac{Q_H}{0.21} \quad (3)$$

where ECSA is the electrochemical active surface area in cm², Q_H (mC) is the charge from the oxidation of adsorbed hydrogen in the hydrogen region of the CVs, 0.21 mC/cm² is the electrical charge associated with monolayer adsorption of hydrogen on Pt. The ECSA of Pt/Ti₉O₁₇ and Pt/C are calculated as 1.02 and 0.33 cm², respectively. The specific ECSA of the Pt/Ti₉O₁₇ and Pt/C are further calculated and obtained as 10.2 and 5.04 m²/g, respectively.

An RDE voltammetric technique is extremely useful in evaluating the catalytic activity of electrocatalysts for ORR. Figure 4 illustrates hydrodynamic voltammograms obtained for the ORR at the state-of-the-art Pt/C or Pt/Ti₉O₁₇-modified electrodes at different rotation rates speed of 400–2000 rpm in O₂-saturated 0.5 M H₂SO₄ electrolyte solution at a scan rate of 10 mVs^{−1}.

The transferred electron number per oxygen molecule involved in the ORR at the Pt/C and Pt/Ti₉O₁₇ electrocatalysts was determined by the Kouteckey-Levich equation (Equation (4)) in which i_L is the Levich current and is expressed by Equation (5))

$$\frac{1}{i_l} = \frac{1}{i_k} + \frac{1}{i_L} \quad (4)$$

$$i_L = 0.62nFAD_{O_2}^{2/3}\nu^{-1/6}C_{O_2}\omega^{1/2} \quad (5)$$

where n is the number of electrons transferred per oxygen molecule, F is the Faraday constant (96,485 C mol^{−1}), A is a geometric area of the electrode (0.196 cm²), D_{O_2} is the diffusion coefficient of O₂ (1.93 × 10^{−5} cm² s^{−1}), ν is the kinetic viscosity of the solution (1.009 × 10^{−2} cm² s^{−1}), and C_{O_2} is the concentration of dissolved O₂ in solution (1.26 × 10^{−3} mol L^{−1}) [32].

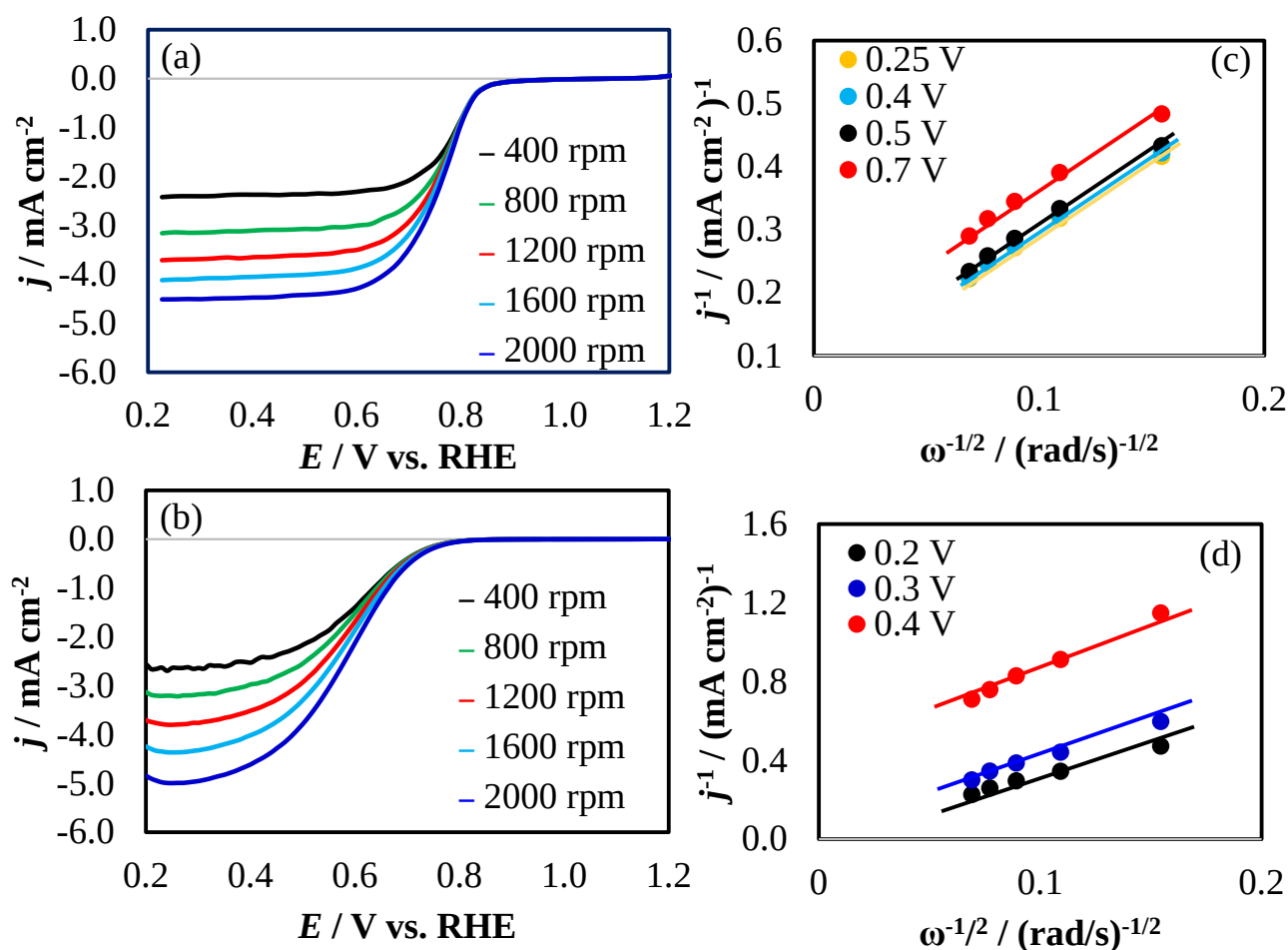


Figure 4. Hydrodynamic voltammograms obtained at the disk electrodes coated with (a) state-of-the-art Pt/C catalyst and (b) Pt/Ti₉O₁₇ catalysts in O₂-saturated 0.5 M H₂SO₄ solution at scan rate of 10 mV s⁻¹ at various rotation rates of 400 to 2000 rpm. Koutecky–Levich plots at various potentials obtained with (c) state-of-the-art Pt/C catalyst and (d) Pt/Ti₉O₁₇.

As shown in Figure 4c,d, the Koutecky–Levich plots of i_l^{-1} versus $\omega^{-1/2}$ at various potentials for the voltammograms of Figure 4a,b gave the straight lines the slopes that are equal to that expected for four-electron ORR, and the values of n were found to be 3.98 and 3.94 for the Pt/C, and Pt/Ti₉O₁₇ electrocatalysts, respectively.

The AST of catalysts was performed and shown in Figure 5. Pt/Ti₉O₁₇ was exposed to an accelerated stability test which consists of 12,000 potential cycles in an O₂-saturated solution and was compared to the state-of-the-art Pt/C (Figure 4a,b). In Figure 5a, the current remains almost constant even after 12,000 cycles of degradation indicating the enhanced stability of the catalyst. However, the current significantly decreases with a time of stability testing in the state-of-the-art Pt/C, indicating degradation of catalyst (Figure 5b). The catalyst degradation is evaluated by comparing ORR polarization curves at 1200 rpm and cyclic voltammetry at N₂-saturated H₂SO₄ solution. The onset potential of ORR at Pt/Ti₉O₁₇ (Figure 5c) remains the same before and after the stability. In contrast, the onset potential at Pt/C (Figure 5d) shifted to higher reductive potential after stability confirming the degradation at Pt/C. Furthermore, Figure 5d shows a limiting current being decreased at Pt/C after stability testing, whereas the diffusion-limited current density of Pt/Ti₉O₁₇ in Figure 5c remains unchanged. Platinum dissolution and agglomeration are well-known degradation paths leading to such effects at Pt/C, which suggested carbon itself is not a perfect support material. On the other hand, less than 10 ± 2.5% degradation ORR performance is observed, indicating a good and alternative support material for Pt in

PEMFC application. Further analysis of catalyst degradation is carried out by comparing CVs and ECSA of catalysts before and after the stability study. The CVs obtained at Pt/TiO₁₇ (Figure 5e) were identical when compared with the before and after 12,000 cycles of degradation, whereas a significant difference in CVs was obtained before and after stability at Pt/C (Figure 5f). The indications of catalyst degradation become apparent by calculating the electroactive Pt surface. Figure 6 compares the ECSA losses for both catalysts. The ECSA decreased at Pt/TiO₁₇ by $10 \pm 2\%$ whereas at Pt/C by almost $50 \pm 5\%$ from the initial values. Thus, the decrease of ECSA at the state-of-the-art Pt/C indicates the least stable catalyst during PEMFC operating conditions.

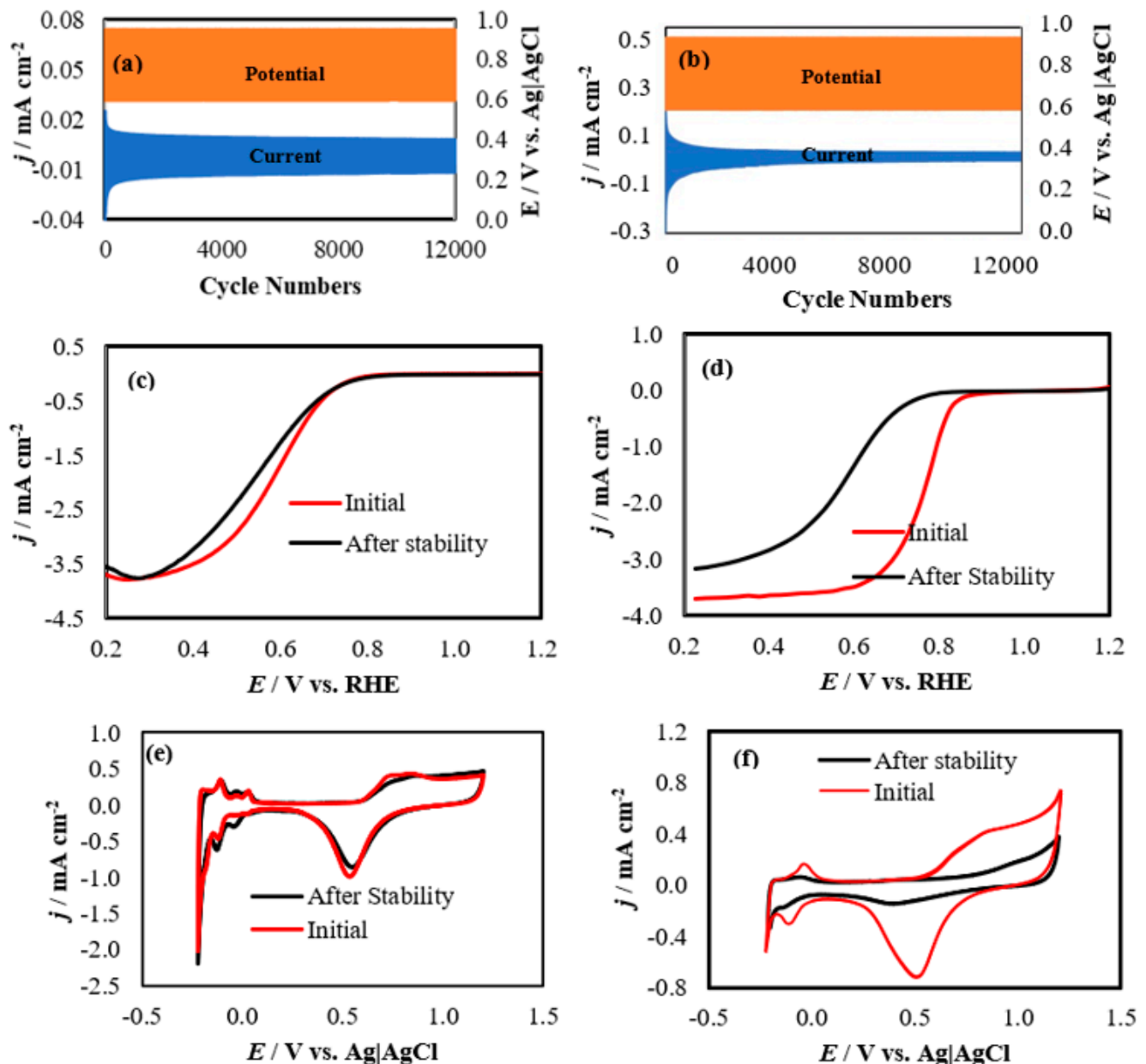


Figure 5. AST studies obtained using the rotating disk electrodes with (a) Pt/TiO₁₇ catalyst and (b) state-of-the-art Pt/C catalyst carried out in O₂-saturated 0.5 M H₂SO₄ solution. Comparison of ORR polarization curves at (c) Pt/TiO₁₇ catalyst and (d) state-of-the-art Pt/C catalyst. Comparison of CVs at (e) Pt/TiO₁₇ catalyst and (f) state-of-the-art Pt/C catalyst before and after stability test.

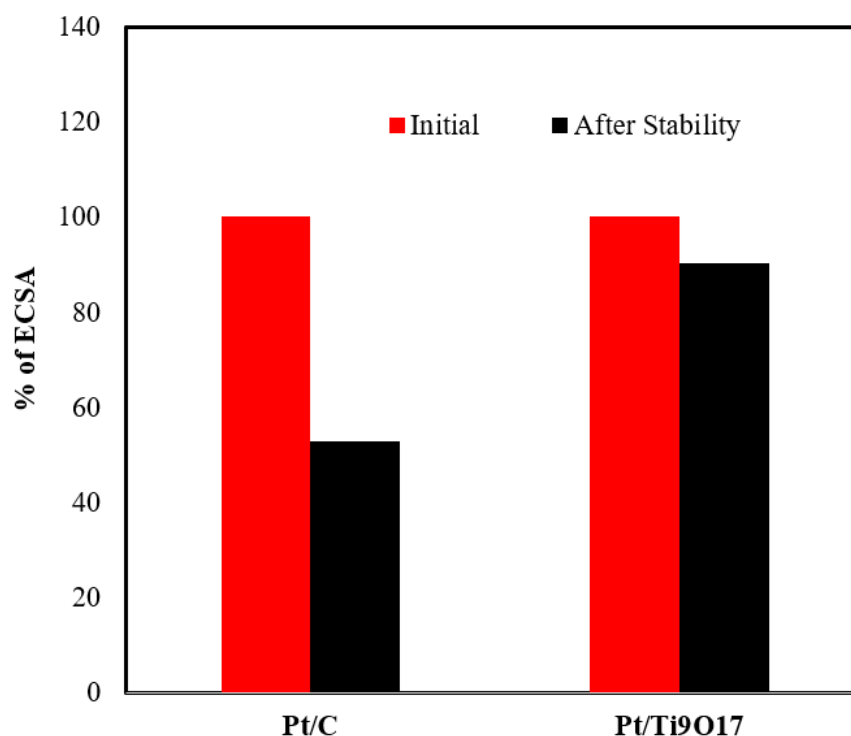


Figure 6. The ECSA before and after stability for state-of-the-art Pt/C catalyst and Pt/Ti₉O₁₇ catalyst.

4. Conclusions

In the present study, we have successfully synthesized a highly stable and corrosion-resistant Magnéli phase titania (Ti₉O₁₇) as a support for the Pt electrocatalyst for PEMFC. Like Pt/C, Pt/Ti₉O₁₇ exhibits the 4e[−] ORR process in O₂-saturated 0.5 M H₂SO₄. The durability of a Pt/Ti₉O₁₇ under the PEMFC operating protocol was evaluated and compared to those of the state-of-the-art Pt/C catalyst. After 12,000 potential cycles, the Pt/Ti₉O₁₇ retained 90 ± 2% of its ECSA, while the state-of-the-art Pt/C catalyst retained only 50 ± 5% of its ECSA. In addition, the comparison of ORR polarization curves before and after the AST study also supports the excellent stability of the synthesized catalyst. These results indicate that the Pt/Ti₉O₁₇ exhibits significantly higher durability due to the fabricated support material of its higher corrosion resistance property.

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