Pt/C-TiO₂ as Oxygen Reduction Electrocatalysts against Sulfur Poisoning

Yuxin Liu 1,2, Jing Ye 2, Fanpeng Kong 2, Chunyu Du 2, Pengjian Zuo 2, Lei Du 3,* and Geping Yin 2,*

1 College of Chemical and Environmental Engineering, Yancheng Teachers University, Yancheng 224051, China; liuyuxin_hit@126.com
2 School of Chemistry and Chemical Engineering, Harbin Institute of Technology, 92 West Dazhi St., Harbin 150001, China; ching_yip@foxmail.com (J.Y.); fpkong@hit.edu.cn (F.K.); cydu@hit.edu.cn (C.D.); zuopj@hit.edu.cn (P.Z.)
3 Huangpu Hydrogen Innovation Center, School of Chemistry and Chemical Engineering, Guangzhou University, Guangzhou 510006, China
* Correspondence: lei.du@gzhu.edu.cn (L.D.); yingeping@hit.edu.cn (G.Y.)

Abstract: Proton exchange membrane (PEM) fuel cells using Pt-based materials as electrocatalysts have achieved a decent performance, represented by the launched Toyota Mirai vehicle. The ideal PEM fuel cells consume stored pure hydrogen and air. However, SO₂, as a primary air contaminant, may be fed along with air at the cathode, leading to Pt site deactivation. Therefore, it is important to improve the SO₂ tolerance of catalysts for the stability of the oxygen reduction reaction (ORR).

In this work, we develop the Pt/C-TiO₂ catalyst against SO₂ poisoning during ORR. Impressively, the hybrid Pt/C-TiO₂ catalyst with 20 mass % TiO₂ shows the best ORR and anti-toxic performance: the kinetic current density of ORR is 20.5% higher and the degradation rate after poisoning is 50% lower than Pt/C. The interaction between Pt and TiO₂ as well as the abundant hydroxyl groups on the surface of TiO₂ are both revealed to account for the accelerated removal of poisonous SO₂ on Pt surfaces.

Keywords: electrocatalysis; oxygen reduction reaction; sulfur dioxide; durability

1. Introduction

The PEM fuel cell has been considered as one of the most promising automobile power supplies owing to its high energy efficiency and environmental benefits [1–3]. Delightfully, the first-generation Toyota Mirai has provided an excellent example, using PtCo as a cathode catalyst, achieving a max power with 114 kW and an endurance mileage of up to 502 km. However, the widespread implementation of PEM fuel cells is facing a greatly challenging poisoning/degradation problem caused by impurities such as SO₂ and NOₓ in the air, which is ideally supplied directly to the cathodes [4,5]. In particular, SO₂ can strongly adsorb onto the Pt surface and deactivate the active sites for the oxygen reduction reaction (ORR), leading to the degradation of ORR performance [6–13]. For example, it has been reported that the continuous feeding of 2.5 ppm SO₂/air mixture for 45 h at the cathode significantly reduced the fuel cell performance by 53% and, importantly, the subsequent continuous clean air feeding for 20 h could not completely recover the performance [14]. This is because the widely accepted Pt/C catalysts are not efficient enough to remove the Sₓ species once the coverage is higher than 14%, where up to 95% of mass activity can be lost [15]. In addition, an extremely harsh potential range of 1.2 V~1.5 V is required to completely oxidize SOₓ into water-soluble SO₄²⁻ and/or HSO₄⁻, which is much higher than the working potential of a PEM fuel cell (0.6 V~0.8 V) [6,16,17]. In this regard, the poisoning SO₂ species is almost irreversible under the normal operating conditions of a PEM fuel cell [18]. This fact triggers us to explore innovations in developing advanced anti-poisoning catalysts.
Numerous efforts have been made to prevent Pt-based catalysts from SO$_2$ poisoning [19]. For example, Baturina and coworkers [20,21] found that the adsorbed SO$_2$ is more easily oxidized and removed on Pt$_3$Co/C than Pt/C, although the alloying Pt$_3$Co/C catalyst is more sensitive to the poisoning (The same concentration of SO$_2$ has a more serious effect on the ORR performance of Pt$_3$Co/C). They found that H$_2$O is more likely to decompose into hydroxyl (-OH) on Pt$_3$Co/C, which is beneficial for accelerating the electro-oxidation of SO$_2$. In addition, Xu et al. [22] found that the SO$_2$-poisoned 5 mass % WO$_x$–Pt/C can cause a higher loss of SO$_2$ than commercial Pt/C after the first potential cycling up to 1.5 V, which might be due to the synergistic effect between WO$_x$ and Pt. The OH group on the hydrophilic WO$_x$ surface and the hydrogen spillover effect promote the electro-oxidation of sulfur-containing species. In their latter work, the Pt/CoO$_2$/C catalyst was prepared by one-pot synthesis, enhancing the oxygen migration and thus improving SO$_2$ electro-oxidation and ORR activity [23,24]. In our previous work, we found that Ru efficiently modified the electronic structure of Pt in PtRu alloy catalysts, leading to a weaker interaction between Pt and SO$_2$ [25]. In this work, we will focus on the effect of metal oxides to the ORR performance and SO$_2$ tolerance of Pt.

To tone-up the positive effects of oxidative hydroxyl and synergy, we herein develop a hybrid Pt/C-TiO$_2$ catalyst against SO$_2$ poisoning during ORR. The selection of TiO$_2$ is based on its high hydrophilicity and outstanding chemical and electrochemical stability, as well as strong interaction with the Pt component [26–33]. Importantly, based on the above discussions, the abundant hydroxyl groups (-OH) on the hydrophilic TiO$_2$ surface may benefit poisonous sulfur removal. Accordingly, the electro-oxidation of SO$_2$ is significantly accelerated on such a Pt/C-TiO$_2$ catalyst to reduce the SO$_2$ poisoning. To our knowledge, the effect of TiO$_2$ on suppressing SO$_2$ poisoning of Pt-based ORR catalysts has not been reported. In this work, our hybrid Pt/C-TiO$_2$ catalysts have higher ORR activity and better sulfur tolerance compared to traditional Pt/C.

2. Results and Discussion

2.1. Characterization of Catalysts

Figure 1 shows the X-ray diffraction (XRD) patterns of the as-prepared Pt/C, Pt/C-TiO$_2$ and TiO$_2$ nanoparticles. For the Pt/C sample, the broad X-ray diffraction peak at 20$^\circ$~30$^\circ$ corresponds to the amorphous structure of XC-72 carbon black, while the peaks at 39.8$^\circ$, 46.2$^\circ$, 67.5$^\circ$, and 81.3$^\circ$ correspond to Pt(111), (200), (220), and (311) facets, respectively (JCPDS No. 04-0802). The commercial TiO$_2$ sample shows sharp peaks, which can be indexed to the anatase TiO$_2$ (JCPDS No. 21-1272). The XRD pattern of Pt/C-TiO$_2$ has the X-ray diffraction peaks of both Pt and TiO$_2$. The above facts demonstrate that the Pt/C and Pt/C-TiO$_2$ were synthesized successfully.

As the high-resolution transmission electron microscopy (HRTEM) image in Figure 2a shows, the Pt nanoparticles are uniformly dispersed on the carbon supports with an average size of about 2.74 nm (Figure S1). A small Pt particle size and uniform dispersion potentially ensure good catalytic performance [34]. Figure 2b shows TEM images of the as-prepared Pt/C-TiO$_2$ catalyst. The lattice fringes of 0.35 nm (red tags) and 0.22 nm (yellow tags) are assigned to the TiO$_2$ (101) plane and the Pt (111) plane, respectively. It can be seen that the TiO$_2$ and Pt particles are well contacted with each other.

2.2. Electrocatalytic Performance

The cyclic voltammogram (CV) and linear sweep voltammetry (LSV) curves of all pristine catalysts (before poisoning) are shown in Figure 3a,b, respectively. The electrochemical surface areas (ECSAs) of all the catalysts were calculated based on the H$_2$ adsorption/desorption region at 0~0.3 V in CV curves. All the relevant data recorded and calculated from electrochemical measurement are listed in Table 1.
Figure 1. XRD patterns of Pt/C, commercial TiO\textsubscript{2} and Pt/C-20TiO\textsubscript{2} catalysts.

As the high-resolution transmission electron microscopy (HRTEM) image in Figure 2a shows, the Pt nanoparticles are uniformly dispersed on the carbon supports with an average size of about 2.74 nm (Figure S1). A small Pt particle size and uniform dispersion potentially ensure good catalytic performance [34]. Figure 2b shows TEM images of the as-prepared Pt/C-20TiO\textsubscript{2} catalyst. The lattice fringes of 0.35 nm (red tags) and 0.22 nm (yellow tags) are assigned to the TiO\textsubscript{2} (101) plane and the Pt (111) plane, respectively. It can be seen that the TiO\textsubscript{2} and Pt particles are well contacted with each other.

Figure 2. (a) TEM images of Pt/C and (b) Pt/C-20TiO\textsubscript{2} catalysts.

The results show that the addition of TiO\textsubscript{2} has little effect on the ECSA of the Pt/C catalyst. Compared with that of Pt/C, the current peak, representing the oxygen reduction of the Pt/C-TiO\textsubscript{2} catalysts, shifts positively when TiO\textsubscript{2} \textless= 30\%; Pt/C-20TiO\textsubscript{2} has the most positive oxygen reduction peak, which likely indicates the best ORR activity, consistent with the LSV results in Figure 3b. The activity towards ORR is improved by increasing TiO\textsubscript{2} content and then started to decrease after reaching a maximum value, i.e., Pt/C-20TiO\textsubscript{2}. Too much TiO\textsubscript{2} (\textgeq 30 mass %) hinders the ORR activity, which is due to the low electron conductivity of TiO\textsubscript{2}. On the other hand, the half-wave potential ($E_{1/2}$) of Pt/C-20TiO\textsubscript{2} is 0.867 V, presenting an increase by 0.014 V compared with Pt/C (0.853 V), and the $i_k$ @ 0.9 V is 2.337 mA/cm\textsuperscript{2}, 20.5\% higher than Pt/C (1.939 mA/cm\textsuperscript{2}). Based on the Koutechy–Levich (K–L) equation (see Section 3.3), the ORR polarization curves of Pt/C-20TiO\textsubscript{2} were...
measured at different rotation speeds (Figure S2a). The charge transfer electrons \( (n) \) of Pt/C-20TiO\(_2\) can be derived from the slopes of the liner K-L plot (Figure S2b), which are 3.89, 3.87, 3.87, and 3.86 at 0.75 V, 0.7 V, 0.65 V, and 0.6 V, respectively, indicating the four-electron reaction pathway of ORR. This fact demonstrates the positive effect of TiO\(_2\) for ORR activity.

![Figure 3](image)

**Figure 3.** The (a) CV and (b) LSV curves of all pristine catalysts (before poisoning).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pristine ECSA ( (\text{m}^2 \text{g}_{\text{Pt}}^{-1}) )</th>
<th>( E_{1/2} ) (V)</th>
<th>( i_k @ 0.9 \text{ V} ) (mA cm(^{-2}))</th>
<th>SO(<em>2) Poisoned ECSA ( (\text{m}^2 \text{g}</em>{\text{Pt}}^{-1}) )</th>
<th>( E_{1/2} ) (V)</th>
<th>( i_k @ 0.9 \text{ V} ) (mA cm(^{-2}))</th>
<th>Negative Shift of ( E_{1/2} ) after Poisoning (mV)</th>
<th>Loss of ( i_k ) @ 0.9 V after Poisoning</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/C</td>
<td>97.07</td>
<td>0.853</td>
<td>1.939</td>
<td>27.06</td>
<td>0.872</td>
<td>0.624</td>
<td>71</td>
<td>67.8%</td>
</tr>
<tr>
<td>Pt/C-5TiO(_2)</td>
<td>97.84</td>
<td>0.855</td>
<td>2.042</td>
<td>26.55</td>
<td>0.880</td>
<td>1.175</td>
<td>55</td>
<td>42.5%</td>
</tr>
<tr>
<td>Pt/C-10TiO(_2)</td>
<td>102.04</td>
<td>0.858</td>
<td>2.172</td>
<td>28.32</td>
<td>0.899</td>
<td>1.424</td>
<td>49</td>
<td>34.4%</td>
</tr>
<tr>
<td>Pt/C-20TiO(_2)</td>
<td>101.46</td>
<td>0.867</td>
<td>2.337</td>
<td>25.99</td>
<td>0.814</td>
<td>1.517</td>
<td>53</td>
<td>35.1%</td>
</tr>
<tr>
<td>Pt/C-30TiO(_2)</td>
<td>99.11</td>
<td>0.86</td>
<td>2.210</td>
<td>29.82</td>
<td>0.775</td>
<td>0.801</td>
<td>85</td>
<td>63.7%</td>
</tr>
<tr>
<td>Pt/C-40TiO(_2)</td>
<td>95.11</td>
<td>0.855</td>
<td>1.884</td>
<td>26.81</td>
<td>0.736</td>
<td>0.716</td>
<td>119</td>
<td>62.0%</td>
</tr>
</tbody>
</table>

The first CV scans of each catalyst after poisoning in Ar-saturated 0.1 M HClO\(_4\) solution are shown in Figure 4a, where the ECSA of all the catalysts decreases in a similar way because the strongly adsorbed SO\(_2\) blocks the active site of Pt. In addition, clear oxidation peaks are observed in the potential range of 0.8 V–1.5 V, due to the electrochemical oxidation of SO\(_2\). Notably, there is a negative shift in the SO\(_2\) oxidation peak of Pt/C-TiO\(_2\) catalysts compared with Pt/C, indicating the higher activity of Pt/C-TiO\(_2\) catalysts to oxidize SO\(_2\). Particularly, the Pt/C-20TiO\(_2\) has the largest negative shift by about 50 mV in SO\(_2\) oxidation, as shown in Figure 4b. The oxide reduction potential region of Figure 4b is magnified and shown in Figure 4c to compare the catalytic performance of Pt/C and Pt/C-20TiO\(_2\) before and after poisoning. It is clear that the reduction peaks of Pt/C-20TiO\(_2\) before or after poisoning all positively shift compared with the Pt/C catalyst, indicating that the Pt/C-20TiO\(_2\) has a better electrocatalytic performance to reduce oxygen-bearing species than Pt/C at initial and after sulfur poisoning.
The first CV scans of each catalyst after poisoning in Ar-saturated 0.1 M HClO₄ solution are shown in Figure 5a. After SO₂ poisoning, the ORR activity of all catalysts is decreased, although the Pt/C-20TiO₂ catalyst still has the best ORR activity. The $i_\text{kHz}$ at 0.9 V comparison between the fresh and poisoned catalysts is shown in Figure 5b. With the addition of TiO₂, the decrease percentage of kinetic current density is significantly lowered. The Pt/C-10TiO₂ and Pt/C-20TiO₂ catalysts have the smallest activity decay by only 34.4% and 35.1%, respectively, in contrast to 67.8% for Pt/C. Table 1 shows that the $E_{1/2}$ of Pt/C-20TiO₂ went down by 53 mV negatively after poisoned, much lower than the 71 mV of Pt/C. All this indicates that the SO₂ tolerance of Pt/C-20TiO₂ is greatly improved than Pt/C.

![Figure 4. CV curves in Ar-saturated 0.1 M HClO₄ solution of (a) all catalysts after SO₂ poisoning, (b) Pt/C and Pt/C-20TiO₂ before and after poisoning, and (c) corresponding magnification at oxide reduction potential region.](image)

**Figure 4.** CV curves in Ar-saturated 0.1 M HClO₄ solution of (a) all catalysts after SO₂ poisoning, (b) Pt/C and Pt/C-20TiO₂ before and after poisoning, and (c) corresponding magnification at oxide reduction potential region.

The LSV curves of ORR after SO₂ poisoning are shown in Figure 5a. After SO₂ poisoning, the ORR activity of all catalysts is decreased, although the Pt/C-20TiO₂ catalyst still has the best ORR activity. The $i_\text{kHz}$ at 0.9 V comparison between the fresh and poisoned catalysts is shown in Figure 5b. With the addition of TiO₂, the decrease percentage of kinetic current density is significantly lowered. The Pt/C-10TiO₂ and Pt/C-20TiO₂ catalysts have the smallest activity decay by only 34.4% and 35.1%, respectively, in contrast to 67.8% for Pt/C. Table 1 shows that the $E_{1/2}$ of Pt/C-20TiO₂ went down by 53 mV negatively after poisoned, much lower than the 71 mV of Pt/C. All this indicates that the SO₂ tolerance of Pt/C-20TiO₂ is greatly improved than Pt/C.

![Figure 5. (a) The LSV ORR curves of SO₂ poisoned catalysts; (b) the kinetic current density at 0.9 V of fresh and SO₂−poisoned catalysts.](image)

**Figure 5.** (a) The LSV ORR curves of SO₂ poisoned catalysts; (b) the kinetic current density at 0.9 V of fresh and SO₂−poisoned catalysts.

### 2.3. Mechanism of SO₂ Tolerance

The X-ray photoelectron spectroscopy (XPS) spectra of the O 1s, Ti 2p and Pt 4f regions in TiO₂, Pt/C, and Pt/C-20TiO₂ are shown in Figure 6. As shown in the O 1s region (Figure 6a), the peaks at 533.5 ± 0.1 eV, 532.2 ± 0.1 eV and 530.6 ± 0.1 eV are assigned to physically absorbed water (O1), chemisorbed OH species (O2), and lattice oxygen in TiO₂ and/or PtO (O3) [26,35]. In addition, it can be seen that the Ti 2p binding energy of Pt/C-20TiO₂ has a negative shift by 0.4 eV compared with Pt/C (Figure 6b). The Pt 4f regions for Pt/C and Pt/C-20TiO₂ can be fitted into three sets of doublets (Figure 6c). For the Pt/C, Pt 4f peaks at 71.4 eV and 74.7 eV are assigned to Pt (0), 72.8 eV and 76.1 eV to Pt (II) in PtO or Pt(OH)₂-like species, and 74.0 eV and 77.3 eV to Pt(IV) in PtO₂. Interestingly, the binding energy of the Pt/C-20TiO₂ catalyst is negatively shifted by 0.3 eV compared to the Pt/C catalyst, indicating an electronic interaction between Pt and TiO₂.
2.3. Mechanism of SO2 Tolerance

The X-ray photoelectron spectra in Figure 6 (a) O 1s region of TiO2, Pt/C and Pt/C–20TiO2; (b) Ti 2p XPS of TiO2 and Pt/C–20TiO2; (c) Pt 4f XPS of Pt/C and Pt/C–20TiO2.

The electron transfer from TiO2 to Pt increases the electron density of Pt, which was reported as a necessity for effective ORR [36]. In addition, the binding energy between Pt and OH-like oxygen-containing species is weakened, which accelerates the reaction of O, OH, and H+ to generate H2O and improves the ORR activity [37,38]. Jaksic et al. [39] found that in aqueous media, OH on the surface of metal oxides such as WO3 and TiO2 can be transferred to the Pt surface to form Pt-OH, which is the so-called spillover effect. Reasonably, such an OH spillover effect of TiO2 will repel the OH groups on Pt, leading to decreased binding energy between OH and Pt and promoting ORR activity [40]. On the other hand, the electronic interaction between Pt and TiO2 is able to weaken the adsorption of poisoning species on Pt surfaces [25,41]. At the same time, the spillover effect of oxidative OH on the TiO2 surface plays a significant role in promoting the electro-oxidation (removal) of SO2 [22]. Figure 7 is provided to illustrate this mechanism. For the Pt/C-TiO2 catalyst: Pt provides electrocatalytic active sites for oxygen reduction; C supports Pt nanoparticles and conducts electrons; and TiO2 modifies the electronic structure of Pt to enhance the ORR activity and SO2 tolerance.

3. Materials and Methods

3.1. Chemicals and Materials Characterization

Chloroplatinic acid (H2PtCl6, Sinopharm Chemical Reagent), Vulcan carbon XC-72 (Cabot Corp, Boston, MA, USA), TiO2 nanoparticles (25 nm, anatase, Aladdin, Shanghai, China), perchloric acid (HClO4, Aladdin, Shanghai, China), anhydrous sodium sulfate (Na2SO3, Dupont, Eleutherian Mills, DE, USA), and 5.0 wt % Nafion aqueous solution (Dupont, Eleutherian Mills, DE, USA) were of analytical grade and used as received if not
specified. Deionized water (18.2 MΩ cm, Mill-Q Corp, Darmstadt, Germany) was used in all of the experiments.

TEM and HRTEM images were taken on JEOL JEM-2100 with an acceleration voltage of 300 kV. The morphologies and crystal structure of the Pt/C, Pt/C-TiO₂ catalyst and TiO₂ nanoparticles were characterized by XRD (Netherlands, Panalytical X’PERT) using Cu Kα radiation. XPS measurements were performed by a Physical Electronics PHI model 5700 instrument with an electron energy analyzer, with half-spherical precision using Al Kα radiation (1486.6 eV). The binding energy of all samples was calibrated vs. the C 1s value of 284.6 eV.

3.2. Synthesis of Catalysts

The Pt/C catalyst (20 mass % Pt) was prepared by the microwave-assisted polyol reduction method [42]. Briefly, 40 mg Vulcan XC-72 carbon black was well-dispersed into 60 mL ethylene glycol (EG) and isopropanol (V/V = 4:1) under ultrasonic treatment for 2 h. Then H₂PtCl₆-EG solution was added to the slurry and stirred constantly for 2 h. Next, 1 mol/L NaOH-EG solution was dropped into the slurry under continuous stirring until the pH was stable at 12. Argon was injected into the slurry for 20 min to remove oxygen, which was then placed in a microwave oven (2450 MHz, 800 W) and heated for 2 min. After the solution was cooled down to room temperature, a certain amount of dilute nitric acid was added to pH = 3, followed by stirring for 12 h. After washing with plenty of boiling ultra-pure water (Milli-Q, 18 MΩ cm), the Pt/C catalyst was dried in a vacuum oven at 70 °C for 12 h.

The Pt/C catalyst ink was prepared by dispersing 5 mg Pt/C catalyst into a mixture of 5 µL of 5 wt.% Nafion solution, 1.25 mL isopropanol, and 3.75 mL ultra-pure water. For the hybrid Pt/C-TiO₂ catalyst ink, a certain amount of TiO₂ nanoparticles were first dispersed in 3.75 mL ultra-pure water, prior to adding and dispersing 5 mg Pt/C, 5 µL Nafion solution, and 1.25 mL isopropanol. The hybrid catalysts were labeled as Pt/C-5TiO₂, Pt/C-10TiO₂, Pt/C-20TiO₂, Pt/C-30TiO₂, and Pt/C-40TiO₂ using different TiO₂ contents of 5, 10, 20, 30, and 40 mass %.

3.3. Electrochemical Measurements

All electrochemical measurements were carried out in a three-electrode system with an electrolyte of 0.1 mol/L HClO₄ aqueous solution at room temperature, using the glassy carbon rotating-disk electrode (GC-RDE, 5 mm in diameter) as the working electrode, a saturated Ag-AgCl electrode as the reference electrode, and a piece of Pt foil (1 cm²) as the counter electrode. 10 µL of catalyst ink was dropped onto the polished GC-RDE. Then the electrodes were air-dried at room temperature. The catalyst loading was about 10 µg/cm².

The ECSA of the catalyst is calculated based on the charge number of H adsorption or desorption, as shown in Equation (1).

\[
\text{ECSA} = \frac{Q_H}{0.21 \times 10^{-3} \times m_{Pt}} \tag{1}
\]

where \(Q_H\) (C) represents the charge number of H adsorption or desorption and can be obtained by integrating the CV curve in Ar-saturated 0.1 mol L⁻¹ HClO₄ solution between 0.05 and 0.4 V; and \(m_{Pt}\) (g) is the Pt load in the catalyst. Assuming there is a one-to-one relationship between the Pt atom and H atom of the hydrogen monatomic layer on the Pt/C catalyst, the charge amount of the hydrogen monatomic layer on the Pt/C catalyst surface is 210 µC cm⁻².

Before recording ORR activity, ultra-pure argon gas was injected into the electrolyte for 20 min to remove dissolved oxygen. CV scans were then performed at the scan rate of 50 mV s⁻¹ in a potential range of 0.05 V~1.5 V for 10 cycles at room temperature. The ORR activity of the catalyst was then measured by LSV from 0.05 V to 1 V at a scan rate of 10 mV s⁻¹ at 1600 rpm in O₂-saturated 0.1 mol/L HClO₄ solution. The kinetic current
density at 0.9 V and transferred electron number were calculated from the ORR polarization following the Koutechy–Levich (K–L) equation, Equation (2).

\[
\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_d} = \frac{1}{i_k} + \frac{1}{0.62nFAD^{2/3}\omega^{1/2}ν^{−1/6}c}
\]  

(2)

where \( i_k \) and \( i_d \) are the kinetic current density and limited diffusion current density, \( n \) is the number of electrons transferred, \( F \) is the Faraday constant \((96,487 \text{ C mol}^{-1})\), \( A \) is the geometric surface area of the RDE, \( c \) is the bulk concentration of \( \text{O}_2 \) \((2.64 \times 10^{-4} \text{ mol cm}^{-3})\), \( D \) is the diffusion coefficient of \( \text{O}_2 \) \((1.93 \times 10^{-5} \text{ cm}^2 \text{ S}^{-1})\), \( ν \) is the kinematic viscosity of the solution \((0.01 \text{ cm}^2 \text{ S}^{-1})\), and \( ω \) is the angular velocity. The half-wave potential \((E_{1/2})\) is read from the ORR curve of the catalyst, which is the potential corresponding to the half of the limited diffusion current density.

The poisoning of catalysts was carried out by immersing the working electrode at the potential of 0.65 V for 1 min in a 0.5 mmol/L \( \text{Na}_2\text{SO}_3 \) + 0.1 mol/L \( \text{HClO}_4 \) electrolyte. Then, the GC-RDE was rinsed with ultra-pure water and transferred to a fresh 0.1 mol/L \( \text{HClO}_4 \) electrolyte without \( \text{SO}_2 \). The ORR activity of the poisoned electrode was evaluated in an \( \text{O}_2 \)-saturated 0.1 mol/L \( \text{HClO}_4 \) electrolyte using LSV at 1600 rpm. To investigate the oxidation behavior of adsorbed \( \text{SO}_2 \), a CV scan was performed between 0.05 V and 1.5 V for 10 cycles at a sweep rate of 50 mV/s. All of the potentials were reported with respect to the reversible hydrogen electrode (RHE) in this work.

4. Conclusions

Hybrid Pt/C-TiO\(_2\) catalysts were prepared by mixing Pt/C catalyst and TiO\(_2\) nanoparticles. By adding TiO\(_2\), the ORR performances of fresh and SO\(_2\)-poisoned catalysts were all improved compared to the Pt/C and the activity loss caused by SO\(_2\) poisoning was remarkably reduced. Our detailed observations indicate that the improved SO\(_2\) tolerance is due to the accelerated electro-oxidation of SO\(_2\) in the presence of optimal TiO\(_2\). We suggest that the electronic interaction between Pt and TiO\(_2\) and the OH spillover effect on TiO\(_2\) might be crucial for not only enhancing the ORR activity, but also removing the poisoning SO\(_2\). These results indicate that the TiO\(_2\) modified Pt/C catalyst is a desired ORR catalyst against sulfur poisoners in PEM fuel cells.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/catal12050571/s1, Figure S1: TEM images of Pt/C and particle size distributions; Figure S2: The ORR polarization curves of Pt/C-20TiO\(_2\) measured at different electrode rotation speeds and the K-L plots from the polarization curve.

Author Contributions: Synthesis and characterization, Y.L. and J.Y.; electrocatalytic experiments, Y.L. and F.K.; supervision, L.D. and C.D.; project administration, G.Y. and P.Z.; writing, Y.L. and L.D.; proofread, G.Y. and L.D. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Key Research and Development Program of China (Program No.2016YFB0101207), Natural Science Research Project of Jiangsu Higher Education Institutions (Grant No.20KJA530004, 21KJA530004), Excellent scientific research and innovation team project of Yancheng Teachers University, and the Outstanding Youth Project of Guangdong Provincial Natural Science Foundation (Grant No. 2022B1515020020).

Data Availability Statement: Data are available in the main text.

Acknowledgments: We acknowledge the financial support from National Key Research and Development Program of China (Program No.2016YFB0101207), Natural Science Research Project of Jiangsu Higher Education Institutions (Grant No.20KJA530004, 21KJA530004), Excellent scientific research and innovation team project of Yancheng Teachers University, and the Outstanding Youth Project of Guangdong Provincial Natural Science Foundation (Grant Number: 2022B1515020020).

Conflicts of Interest: The authors declare no conflict of interest.
References


10. Awad, M.I.; Saleh, M.M.; Ohsaka, T. Impact of SO2 poisoning of platinum nanoparticles modified glassy carbon electrode on oxygen reduction. J. Power Sources 2011, 196, 3722–3728. [CrossRef]


32. Haidry, A.A.; Fatima, Q.; Mehmood, A.; Shahzad, A.; Ji, Y.; Saruhan, B. Adsorption Kinetics of NO$_2$ Gas on Pt/Cr-TiO$_2$/Pt-Based Sensors. *Chemosensors* 2021, 10, 11. [CrossRef]


41. Lv, Q.; Yin, M.; Zhao, X.; Li, C.; Liu, C.; Xing, W. Promotion effect of TiO$_2$ on catalytic activity and stability of Pt catalyst for electrooxidation of methanol. *J. Power Sources* 2012, 218, 93–99. [CrossRef]