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1	Long-term, Stable, and Improved Oxygen-Reduction Performance of
2	Titania-supported PtPb Nanoparticles
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## 1 Abstract

Long-term, stable, and improved electrocatalytic performance towards oxygen reduction reaction (ORR) were achieved by anatase-type titania (TiO<sub>2</sub>)-supported PtPb nanoparticles (NPs). Organometallic precursors, H<sub>2</sub>PtCl<sub>6</sub>.6H<sub>2</sub>O and Pb(CH<sub>3</sub>COO)<sub>2</sub> were co-reduced using sodium borohydride at ambient temperature to precipitate the PtPb NPs (NiAs-type structure, P63/mmc, a =0.4259 nm; c = 0.5267 nm, average particles size: 3 nm) over the TiO<sub>2</sub> support (PtPb/TiO<sub>2</sub>). PtPb/TiO<sub>2</sub> showed a substantial electrocatalytic activity towards ORR both in terms of the onset potential and the mass activity compared to TiO<sub>2</sub>-supported Pt NPs (Pt/TiO<sub>2</sub>). The onset potential of PtPb/TiO<sub>2</sub> was shifted to high electric potentials by 180 mV compared to Pt/TiO<sub>2</sub>. Also, PtPb/TiO<sub>2</sub> showed a seven-times higher ORR mass activity than Pt/TiO<sub>2</sub>. Neither the onset potential nor the mass activity of PtPb/TiO<sub>2</sub> altered after ORR cycles, whereas those of commercially available Vulcan carbon-supported Pt NPs (Pt/VC; Pt loading: 20 wt.%). largely altered. The PtPb NPs were not agglomerated over the TiO<sub>2</sub> support even after the repeated cycles under electric potential condition, as the result of the strong interactions between the PtPb NPs and the TiO<sub>2</sub> support, but the Pt NPs were significantly agglomerated over the TiO<sub>2</sub>- and the Vulcan carbon supports due to the weak interactions between the Pt NPs and the supports. PtPb/TiO<sub>2</sub> can be a practical cathode material for direct fuel cells in terms of its long-term stability and enhanced catalytic performance.

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#### **1** Introduction

2 Polymer electrolyte membrane fuel cells (PEMFC) have been sought as an alternative power 3 supply to portable electronic appliances and to the combustion engines that depend largely on the fossil fuels.<sup>1-7</sup> The commercialization of PEMFC can effectively mitigate the toxic tailpipe emissions, 4 5 however, is still facing great challenges owing to the large loading of platinum (Pt) in the electrode 6 catalysts and the poor durability through repeated operations. The performance of PEMFC is greatly 7 diminished by the formation of passivation layers on the catalyst surface during the electrode reaction, which blocks the active catalytic sites.<sup>2, 7-12</sup> Indeed, a strong Pt-O or Pt-OH bond is formed on the Pt 8 cathode surface in the oxygen-saturated electrolyte solution of operating fuel cells, which results in 9 high overpotentials for oxygen reduction reaction (ORR).<sup>8,9</sup> Currently, a large amount of Pt ( $\approx 0.4$  mg 10  $cm^{-2}$ ) is required to realize the desired ORR performance.<sup>2,11,13</sup> The mineral resources for Pt are sparse 11 on the earth's crust and their cost has been increasing more than three-fold in the last three decades.<sup>14</sup> 12 Therefore, significant reduction in the ORR overpotential compared to the reversible thermodynamic 13 14 potential, 1.23 V, with a small amount of Pt is one of the possible solutions to put PEMFC into practice.

Pt-based catalysts can be greatly improved in performance by alloying of Pt with the p- (Pb, Bi, 15 16 etc.) or d- (Ti, Ru, Cu, Ni, Co, Rh, Pd, Au, etc.) group elements and widely utilized for petrochemical industries, exhaust purification, and fuel cell applications.<sup>15-23</sup> The enhancement in the catalytic activity 17 of Pt-based alloys is attributed to the bi-functional mechanism, electronic effects, crystal orientations, 18 or favorable interatomic distances between Pt and the counter atoms.<sup>24-28</sup> The authors and their 19 collaborators demonstrated previously that Pt-based intermetallics containing less expensive metals, for 20 instance Pb, Bi, etc., show the enhanced catalytic activities compared to pure Pt for the oxidation of 21 22 methanol, formic acid, etc., and hence can be used as efficient anode materials for fuel cell applications.<sup>15-17,29,30</sup> 23

Pt or Pt-based intermetallics have been finely dispersed as nanoparticles (NPs) on the carbon 24 supports to utilize them as electrode catalysts for fuel cells because the carbon supports have high 25 electric conductivity, large surface area, and favorable electronic interaction with the metal NPs.<sup>31-34</sup> 26 27 However, the Pt- or Pt-based intermetallic NPs can be agglomerated on the carbon supports during long-term operations of fuel cells through the Ostwald ripening due to the weak Van der Walls 28 interactions between the carbon supports and the NPs.<sup>35-39</sup> Also, electrochemical corrosion of carbon 29 (formal potential  $(E^0) = 0.207$  V vs. NHE) promotes detachment of the NPs.<sup>40-42</sup> In addition, the 30 electrochemical corrosion of carbon was accelerated in the presence of Pt.<sup>43,44</sup> The corrosive resistance 31 of the electrode catalyst can be augmented by replacing of carbon into the chemically as well as 32

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electrically resistant materials. The detachment of catalytic centers from the supports can be prevented
 by enhancing of the interactions between the support and the catalytic centers.

3 Recently, transition metal oxides (TiO<sub>2</sub>, CeO<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub>, WO<sub>3</sub>, MoO<sub>3</sub>, ZrO<sub>2</sub>, etc.) are of confocal interest as chemically durable supporting materials for fuel cells.<sup>45-49</sup> Among the various transition 4 5 metal oxides, TiO<sub>2</sub> is one of the promising supporting materials as catalysts support for the electrode catalyst in terms of their abundance, low cost, semiconductivity, and high stability in corrosive 6 environments.<sup>50-53</sup> Moreover, TiO<sub>2</sub>-supported metallic NPs showed the enhanced catalytic activities as 7 the result of strong interactions between the NPs and the TiO<sub>2</sub> support.<sup>54-56</sup> The O-containing moieties 8 formed due to the sluggish reaction of oxygen on the Pt surface, which can be spilled over to the 9 transition metal oxides and thus the active sites are relatively available for further ORR. It has been 10 suggested that the spillover of the O-containing moieties from the catalyst surface is the key factor for 11 the enhancement of ORR performance.57-59 12

In this work, we successfully demonstrated the superior and long-term, stable catalytic activity 13 towards ORR by combining the intermetallic PtPb NPs and the TiO<sub>2</sub> support (PtPb/TiO<sub>2</sub>). Intermetallic 14 PtPb NPs on the TiO<sub>2</sub> support were prepared by co-reduction of Pt- and Pb precursors under Ar-15 16 atmosphere. The formation of intermetallic phase between Pt and Pb was confirmed by powder X-ray 17 diffraction (pXRD) and X-ray photoelectron spectroscopy (XPS). The morphology and dispersivity of the PtPb NPs were determined by transmission electron microscopy (TEM). The loading weight of Pt 18 19 of the catalysts was estimated by inductively coupled plasma mass spectrometry (ICP-MS). The electrocatalytic activity of PtPb/TiO<sub>2</sub> was examined towards ORR and compared with TiO<sub>2</sub>-supported 20 21 Pt NPs (Pt/TiO<sub>2</sub>). The stability of the catalysts was examined by cycling of the electrode materials 22 under electric potential condition and compared with the commercially available Vulcan carbonsupported Pt NPs (Pt/VC; Pt loading: 20 wt.%). 23

## 24 Experimental Section

## 25 Materials

26 The Pt precursor, H<sub>2</sub>PtCl<sub>6</sub>.6H<sub>2</sub>O (99.9 %) and the Pb precursor, Pb(CH<sub>3</sub>COO)<sub>2</sub> (99.9 %) were purchased from Wako pure chemical industries, Ltd., Japan. TiO<sub>2</sub> (anatase, particle size < 25 nm, 27 28 99.7 %) was purchased from Sigma Aldrich. NaBH<sub>4</sub> (99.99 %) was purchased from Sigma Aldrich. 29 Vulcan carbon (VC) (Vulcan XC-72R) and VC-supported Pt (Pt loading: 20 wt. %) were purchased 30 from E-TEK. The C, Pt, and Pb substrates were purchased from Nilaco Corporation Ltd., Japan. The aliphatic alcoholic solution of Nafion (5 wt. %. EW: 1100) was purchased from Sigma Aldrich. 31 32 Anhydrous methanol (99.8 %) was purchased from Sigma-Aldrich. Isopropanol (99.7 %), HCl (35-37 %), and HNO<sub>3</sub> (60-62 %) were purchased from Wako pure chemical industries, Ltd., Japan. H<sub>2</sub>SO<sub>4</sub> 33

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(96 %), was purchased from Kanto Chemical Co. Inc, Japan. All chemicals and organic solvents were
stored under Ar-atmosphere (less than 5 ppm of O<sub>2</sub> and H<sub>2</sub>O). The supports (TiO<sub>2</sub> and VC) were treated
under Ar-atmosphere at 120 °C to remove the adsorbed moisture for 15 h. Water was purified using the

4 Millipore system (resistance 18.2 M $\Omega$  cm at 25 °C)

## 5 Synthesis of intermetallic PtPb NPs on TiO<sub>2</sub>

6 The PtPb NPs were synthesized through a wet-chemical route by co-reduction of the Pt- and Pb 7 precursors using NaBH<sub>4</sub> as a reducing agent. In the synthesis, the stoichiometric amounts of 0.058 mmole of each Pt- (25.90 mg) and Pb precursors (18.96 mg) were dissolved in anhydrous methanol (15 9 mL) and transferred to a double neck round bottom flask without exposing into air. 6 mmole of NaBH<sub>4</sub> 10 (227 mg) was dissolved in anhydrous methanol and then injected to the precursor solutions under Ar-11 atmosphere. The yellow color solutions turned immediately black color upon NaBH<sub>4</sub> injection with vigorous bubbling. The large-sized black color flakes were formed from the solutions and 12 13 agglomerated within 10 min. The solutions were stirred for 15 h to complete the reaction under Ar-14 atmosphere. The black color suspensions were centrifuged for 10 min at 2000 rpm to yield a black 15 color precipitate and then subsequently washed with 20 mL of anhydrous methanol for three times and 16 dried under vacuum. For TiO<sub>2</sub>-supported PtPb NPs, 0.5 g of TiO<sub>2</sub> was suspended in 15 mL of 17 anhydrous methanol for 15 min in a double neck round bottom flask. 0.1 mmole of each Pt- (51.79 mg) and Pb precursors (15.17 mg) were dissolved in 15 mL of anhydrous methanol in the shielded vial 18 19 under Ar-atmosphere and subsequently transferred to the TiO<sub>2</sub> suspensions. The solutions were stirred for 30 min to yield homogeneous pale yellow color solution. 6 mmole of NaBH<sub>4</sub> in anhydrous 20 21 methanol was injected through stainless steel *cannula* without exposing into air. The pale yellow color 22 solutions turned immediately dark gray color solution upon NaBH<sub>4</sub> injection with vigorous bubbling. 23 The products were washed and dried as similar to TiO<sub>2</sub>-free PtPb NPs, which have black to gray color 24 depending upon the amounts of TiO<sub>2</sub>.

## 25 Characterization

pXRD measurements were performed between the diffraction angles  $(2\theta)$  of 5° and 90° with 0.05° increments at a count time of 4 s over the products to characterize the structures using CuKa radiation generated at 40 kV and 30 mA (RIGAKU, RINT ULTIMA III,  $\lambda = 0.15418$  nm). The size of the Pt and PtPb NPs were calculated using Scherrer formula ( $d = 0.89 \ \lambda/\beta \cos\theta$ ) by taking the diffraction peaks of (111) and (102) planes, respectively, where *d* is the particle size,  $\beta$  is the full width at half-maximum for the diffraction peaks. The shape factor, 0.89, was taken by assuming that the particles are in spherical shape. 1 The microscopic observation of the products was performed using a TEM instrument (JEM-2 2010, JEOL, Japan) operated at an accelerating voltage of 200 kV. High-resolution TEM (HR-TEM) 3 observation was performed using a TEM instrument (HF-2000, Hitachi Ltd., Japan) operated at an 4 acceleration voltage of 200 kV. The TEM samples were prepared by dispersing of the products in 5 methanol under sonication for 5 min and dropped gently on carbon film-supported TEM Cu grids 6 (JEOL, 150 mesh) followed by dried under vacuum. The samples were scratched gently from the GC 7 electrode surface for the microscopic observation after long-term test and dispersed on the TEM grids 8 to examine the influence of the electric potential over the catalysts.

9 X-ray photoelectron spectroscopy (XPS) measurements (JEOL, JPS-9010 MC) were performed 10 to examine the chemical states (Pt 4*f* and Pb 4*f*) of the catalyst. MgK $\alpha$  as X-ray source with anodic 11 voltage (10 kV) and current (10 mA) were used for XPS measurements. All XPS spectra of the samples 12 were obtained with a take-off angle at 45° with respect to the specimens by using the pass energies of 13 100 eV and 200 eV for narrow and survey scans, respectively. The XPS specimens were prepared by 14 ultrasonic mixing of VC (1 mg) and the catalyst (3 mg) in methanol (0.5 mL) for 30 min. The resultant 15 solutions were dropped on the carbon substrates and dried under vacuum.

Elemental analysis over the catalysts was performed to evaluate the amounts of Pt using ICP-MS instrument (Agilent, 7700x). 5 mg of the catalysts were digested in aqua regia (0.5 mL) to dissolve Pt and Pb for 15 h. The Pt- and Pb- dissolved aqua regia solutions were filtered by using Millipore filters (Millex, USA). The solutions were then diluted using Milli-Q water. The Pt and Pb calibration lines were prepared using the standard solutions of Pt and Pb (Wako pure chemical industries, Ltd., Japan).

## 22 Oxygen reduction reaction

23 The samples were coated on a GC electrode (diameter = 5 mm) from the catalyst ink prepared 24 by ultrasonic mixing of the Pt or PtPb samples (3 mg) and VC (2 mg) with Milli-Q water (995 µL), isopropanol (250 µL) and Nafion solutions (5 µL) for 1 h. VC was mixed with the catalysts to realize 25 the better electrical conductivity. 12  $\mu$ L of the catalyst ink with the loading weight of 36  $\mu$ gcm<sup>-2</sup> was 26 27 dropped on the cleaned GC electrode and dried under vacuum. In prior to the coating of the catalysts, the GC electrode was polished with 0.05 µm alumina slurry for 10 min and sonicated for 5 min to 28 remove any adsorbed impurities on the GC electrode and dried under Ar-atmosphere. The catalysts-29 coated GC electrode was immersed in 0.1 M aqueous H<sub>2</sub>SO<sub>4</sub> solution for 10 min to attain the rest 30 31 potential with the electrolyte solution before starting the measurements.

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The conventional electrochemical measurements were performed over the catalysts-coated GC electrode in 0.1 M aqueous H<sub>2</sub>SO<sub>4</sub> solutions to evaluate the ORR performance or the stability of the catalyst using an electrochemical instrument (HOKUTO DENKO, Japan, HSV-100). The catalystscoated GC electrode, spiraled Pt wire, and Ag/AgCl (3 M NaCl) was used as working electrode, counter electrode, and reference electrode, respectively. 0.1 M aqueous H<sub>2</sub>SO<sub>4</sub> solution was purged with Ar for 30 min to remove any dissolved O<sub>2</sub> and then saturated with O<sub>2</sub> for 30 min. The catalystscoated electrode was rotated using electrode rotator (HOKUTO DENKO, Japan, HR-30) at 2000 rpm.

8 The long-term performance of the PtPb-coated GC electrode was examined by cycling of the 9 electrode for 50 cycles in  $O_2$ -saturated  $H_2SO_4$  solutions. Both the onset potential (i.e., the potential at 5  $\mu A \mu g_{Pt}^{-1}$ ) and the mass activity of Pt or PtPb catalysts were used to examine the ORR performance. 10 The catalysts-coated electrode was cycled for 500 cycles to examine the influence of electric potential 11 over the catalysts between -0.2 and 1.2 V at a scan rate of 50 mVs<sup>-1</sup> in O<sub>2</sub>-free 0.1 M aqueous H<sub>2</sub>SO<sub>4</sub> 12 solution. After cycling, the CV measurements were performed in O<sub>2</sub>-saturated 0.1 M H<sub>2</sub>SO<sub>4</sub> solution 13 14 and compared the ORR activity. The formation of oxide moieties on the Pt surface of the various catalysts was monitored at various electric potential regions to examine the sluggish ORR kinetics of 15 the catalysts. 16

## 17 Results and discussion

18 Figure 1 shows the pXRD profiles for the products that were prepared from the Pt- and Pb 19 precursors and TiO<sub>2</sub>-support using NaBH<sub>4</sub> as a reducing agent. The pXRD profile for the products using Pt precursors showed the characteristic reflection peaks at 39.8°, 46.2°, 67.5°, 81.3°, and 85.7° 20 that are assigned to (111), (200), (220), (311), and (222) reflection planes, respectively (FCC-type 21 structure,  $Fm\bar{3}m$ , a = 0.3922 nm), corresponding to Pt.<sup>23</sup> The pXRD profile for the products prepared 22 from Pt- and Pb precursors showed the characteristic reflection peaks at 24.1°, 29.1°, 41.0°, 42.2°, 23 52.3°, 56.1°, 60.4°, 68.5°, 72.7°, 76.4°, and 83.8° that are assigned to (100), (101), (102), (110), (201), 24 25 (103), (202), (004), (203), (212), and (114) reflection planes, respectively (NiAs-type structure, P6<sub>3</sub>/mmc, a = 0.4259 nm; c = 0.5267 nm).<sup>15-17</sup> The observed reflection planes clearly revealed the 26 27 formation of intermetallic phase between Pt and Pb. The products that were prepared from the Pband/or Pt precursors on the TiO<sub>2</sub> support also showed the similar characteristic reflection peaks of Pt or 28 29 PtPb marked as asterisks in addition to TiO<sub>2</sub> reflection peaks. These results indicate that intermetallic 30 phase between Pt and Pb can be achieved on the TiO<sub>2</sub> support through a wet-chemical synthesis route at ambient temperature. The average particle size of the Pt- and PtPb NPs was calculated from the 31 32 reflection peak of (111) for Pt and (102) for PtPb using Scherrer formula to be 10 and 7 nm,

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respectively. The average particle size of the Pt- and PtPb NPs on the  $TiO_2$  support was also calculated as similar to support-free NPs to be 3 nm, which are smaller than that of support-free NPs. The calculated particle size of the Pt- and PtPb NPs is consistent with the particle size that was estimated from the TEM images (see the Figures 2*a* and 2*c*). The smaller particle size can be achieved without affecting the formation of intermetallic phase between Pt and Pb by using of the TiO<sub>2</sub> support.



Figure 1. *p*XRD profiles for support-free and TiO<sub>2</sub>-supported Pt and PtPb NPs. *p*XRD profile for TiO<sub>2</sub>
and simulated XRD lines for Pt and PtPb are shown as the reference. The formation of Pt and PtPb NPs
on TiO<sub>2</sub> is shown as asterisks.

TiO<sub>2</sub>-support-free Pt and PtPb NPs were virtually formed as agglomerated clusters (Figure S1), 23 24 however, finely dispersed and discrete NPs were formed on the TiO<sub>2</sub> support in the case TiO<sub>2</sub>-25 supported Pt and PtPb NPs. Figure 2 represents the bright-field TEM images of Pt/TiO<sub>2</sub> and PtPb/TiO<sub>2</sub> 26 in which the Pt and PtPb NPs are observed as dark spots on the  $TiO_2$  support (Figures 2a and 2c). Both 27 the Pt and PtPb NPs are finely dispersed and showed a symmetrical distribution on the TiO<sub>2</sub> support. Fine dispersion as well as symmetrical distribution of the NPs can be achieved by the utilization of 28 oxide-supports.<sup>23,45-49</sup> The particles size calculated from the TEM images (Figures 2a and 2c) are in the 29 30 range between 1 and 6 nm and the average particle size is centered at 3 nm as shown in the histograms (Figures 2b and 2d). The particle size and their distribution of both Pt and PtPb NPs are virtually same 31 32 on the TiO<sub>2</sub> support regardless of the nature of the NPs. The Pt and PtPb NPs were existed solely as ordered structures and were also embedded on the TiO<sub>2</sub> support as shown in the HR-TEM images 33



Figure 2. Bright-field TEM images of Pt/TiO<sub>2</sub> (*a*) and PtPb/TiO<sub>2</sub> (*c*). The particle size distribution of
the Pt (*b*) and PtPb (*d*) NPs on TiO<sub>2</sub> is shown in the histograms. HR-TEM images of Pt/TiO<sub>2</sub> (*e*) and
PtPb/TiO<sub>2</sub> (*f*).

20 Figure 3a shows the XPS spectral profiles for the Pt bulk and PtPb/TiO<sub>2</sub> in the Pt 4f region. The Pt  $4f_{7/2}$  and Pt  $4f_{5/2}$  emission peaks of the Pt bulk surface showed the binding energies for Pt(0) at 70.9 21 and 74.1 eV, respectively. The Pt  $4f_{7/2}$  and Pt  $4f_{5/2}$  emission peaks of PtPb/TiO<sub>2</sub> also showed the similar 22 23 binding energies for Pt(0), however, slightly shifted to a higher binding energy level by 0.3 eV than that of the Pt bulk surface observed at 71.2 and 74.4 eV, respectively. It was ensured that the XPS 24 measurements were free from charging effect by measuring of the binding energy in the C 1s region, 25 26 which was observed at 284.4 eV (Figure S2). The difference in spin-orbit splitting (d) values of both Pt-bulk and PtPb/TiO<sub>2</sub> was calculated to be ~3.4 eV, which are consistent with the reported values.<sup>47,60</sup> 27 28 The observed higher binding energy shift of Pt in PtPb/TiO<sub>2</sub> is due to the formation of intermetallic 29 phase between Pt and Pb on the TiO<sub>2</sub> support, which can be expected to change their electronic 30 structure significantly. Figure 3b shows the XPS spectral profiles for the Pb bulk surface and PtPb/TiO<sub>2</sub> in the Pb 4f region. The surface of the Pb bulk was cleaned by Ar<sup>+</sup>-etching, in prior to the XPS 31 measurements. The Pb  $4f_{7/2}$  and Pb  $4f_{5/2}$  emission peaks of the Pb bulk surface showed the binding 32 energies for Pb(0) at 136.4 and 141.2 eV, respectively. The Pb  $4f_{7/2}$  and Pb  $4f_{5/2}$  emission peaks of 33

1 PtPb/TiO<sub>2</sub> also again showed the similar binding energies for Pb(0), however, shifted to a higher 2 binding energy level by 0.4 eV than that of the surface of Pb bulk observed at 136.8 and 141.6 eV, 3 respectively. The observed binding energies of Pt and Pb of the PtPb NPs were consistent with the reported PtPb-bulk surface.<sup>61</sup> The higher binding energy shift for Pb in PtPb/TiO<sub>2</sub> is due to the change 4 in their electronic structure compared to the Pb bulk as the result of the formation of intermetallic phase 5 6 between Pt and Pb. These results indicate that the electronic structure of Pt and Pb in PtPb/TiO<sub>2</sub> is 7 significantly different than that of their bulk surfaces. In addition to the emission peaks of Pb(0), the Pb  $4f_{7/2}$  and Pb  $4f_{5/2}$  emission peaks also showed the binding energies at 139.3 and 144.2 eV, respectively, 8 for the Pb-oxides.<sup>61</sup> The formation of the Pb-oxides is unavoidable during the nanoparticulation of 9 intermetallic PtPb through a wet-chemical route. The formation of the Pb-oxides has been reported 10 even in the case of bulk intermetallic PtPb synthesis. The Pb-oxides were formed from the Pb NPs, 11 which were not likely involved for intermetallic phase formation with Pt. The formed Pb NPs were 12 13 stable under Ar-atmosphere, however, were oxidized immediately when the Pb NPs are exposed into 14 air.





Figure 3. X-ray photoelectron spectral profiles for the bulk surfaces of Pt and Pb and PtPb/TiO<sub>2</sub> in the regions of Pt 4f(a) and Pb 4f(b).

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Figure 4. The cathodic potential sweeps (solid lines) for  $Pt/TiO_2$  and  $PtPb/TiO_2$  in  $O_2$ -saturated 0.1 M H<sub>2</sub>SO<sub>4</sub> solution at a scan rate of 10 mVs<sup>-1</sup> and at a rotation rate of 2000 rpm. The blank cathodic potential sweeps of these electrodes are shown as dotted lines. The loading weight of the Pt in the catalysts is shown in the parenthesis. The insets show the ORR current measured at 0.3 V and the onset potential for Pt/TiO<sub>2</sub> (blue) and PtPb/TiO<sub>2</sub> (red).

Figure 4 shows the comparison of the ORR catalytic performance of PtPb/TiO<sub>2</sub> and Pt/TiO<sub>2</sub> in 17 O<sub>2</sub>-saturated 0.1 M H<sub>2</sub>SO<sub>4</sub> solution at a sweep rate of 10 mVs<sup>-1</sup>. The ORR catalytic performance was 18 normalized by the loading weight of Pt of the catalysts that was estimated from ICP-MS experiments 19 (supporting information) instead of the electrochemical surface area (ECSA). This is because 20 21 PtPb/TiO<sub>2</sub> showed no peak for hydrogen adsorption and desorption and therefore ECSA can't be determined (Figure S3). The ORR catalytic activity in terms of the onset potential and the mass activity 22 of PtPb/TiO<sub>2</sub> were compared with Pt/TiO<sub>2</sub> as the reference cathode catalysts are shown in the insets. 23 The mass activity of the catalysts was compared in the kinetic-controlled region at 0.3 V. Pt/TiO<sub>2</sub> 24 showed the ORR activity, having the onset potential and the ORR current density measured at 0.3 V is 25 0.43 V and 0.09 mA µg<sub>Pt</sub><sup>-1</sup>, respectively. PtPb/TiO<sub>2</sub> also showed the ORR activity, however, having the 26 substantially higher ORR activity compared to Pt/TiO<sub>2</sub> both in terms of the onset potential as well as 27 the mass activity. The mass activity of PtPb/TiO<sub>2</sub> was measured at 0.3 V is 0.66 mA  $\mu g_{Pt}^{-1}$ , which is 28 approximately seven-times higher than that of Pt/TiO<sub>2</sub> (inset). In addition, the onset potential of 29 PtPb/TiO<sub>2</sub> is shifted by 180 mV and observed at 0.61 V compared to Pt/TiO<sub>2</sub>. The substantial electric 30 potential shift of PtPb/TiO<sub>2</sub> towards a higher electric potential is favorable for cathode catalyst, which 31 32 can reduce the cathodic overpotential significantly. These results indicate that the enhanced ORR



activity of PtPb/TiO<sub>2</sub> compared to Pt/TiO<sub>2</sub> is most likely due to the changes in the electronic structure
 (as evidenced from XPS results)<sup>61</sup> of Pt owing to the formation of intermetallic phase between Pt and
 Pb.



Figure 5. The ORR performance of Pt/VC (*a*), Pt/TiO<sub>2</sub>, (*b*) and PtPb/TiO<sub>2</sub> (*c*) for 50 cycles in O<sub>2</sub>saturated 0.1 M H<sub>2</sub>SO<sub>4</sub> solution at a scan rate of 10 mVs<sup>-1</sup>.

The long-term ORR performance of Pt/TiO<sub>2</sub> and PtPb/TiO<sub>2</sub> was examined and compared with the commercially available Pt/VC, which is critical to realize the practical cathode catalyst for fuel cell applications. The long-term ORR performance was performed solely up to 50 cycles due to the

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1 limitation in the localized concentration of O2 on the electrode surface. The ORR currents were 2 calculated in the kinetic-controlled region at 0.45 V for Pt/VC and 0.3 V for Pt/TiO<sub>2</sub>, PtPb/TiO<sub>2</sub> rather 3 than mass-controlled region. Figure 5a shows the CVs of the Pt/VC electrode in O<sub>2</sub>-saturated 0.1 M 4 H<sub>2</sub>SO<sub>4</sub> solution. The onset potential of Pt/VC is progressively shifted to a lower electric potential 5 region with increasing of the ORR scans. The ORR current density of the Pt/VC electrode at 0.45 V 6 also decreased with increasing of the ORR scans. Figure 5b shows the CVs of the Pt/TiO<sub>2</sub> electrode in 7 O<sub>2</sub>-saturated 0.1 M H<sub>2</sub>SO<sub>4</sub> solution. Both the onset potential and the current density at 0.3 V didn't 8 show any significant changes with increasing of the ORR scans. The PtPb/TiO<sub>2</sub> electrode also didn't 9 show any significant changes both in the onset potential and the current density, however, showed the onset potential at a higher electric potential than that of the  $Pt/TiO_2$  electrode (Figure 5c). In addition, 10 the ORR current density of PtPb/TiO<sub>2</sub> was not changed significantly with increasing of the ORR scans. 11 PtPb/TiO<sub>2</sub> showed the remarkable performance in the ORR activity than that of Pt/TiO<sub>2</sub> as well as the 12 13 commercially available Pt/VC.

110

100

90

80

70

60

50

0 10

ili<sub>cycle#1</sub>×100 (%)

Pt/TiO<sub>2</sub>

PtPb/TiO<sub>2</sub>

20 30 40

ORR cycles (n)

b

Pt/VC

50

а

Pt/VC

Pt/TiO<sub>2</sub>

PtPb/TiO<sub>2</sub>

40

20

30

ORR cycles (n)

10





0.58

0.56

0.54

0.52

0.45

0.44

0.43 0.42

0.63

0.62

0.61

0.60<sup>L</sup> 0

ORR Onset potential (vs. Ag/AgCl, 3 M NaCl) (V)

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As can be seen in more detail in Figure 6, the onset potential of Pt/VC decreased steeply during the initial ORR scans and progressively decreased with further increasing of the ORR scans. The onset potential of Pt/VC is 0.56 V, which is shifted to a lower onset potential by 30 mV and reached to 0.53 V after 50 ORR cycles. It should be noted that the onset potential is strongly depended on the loading weight of the amounts of Pt on a GC electrode (Figure S4). The ORR current density of Pt/VC at 0.45 V in the first ORR scan, decreased steeply with increasing of the ORR scans as shown in Figure 6*b*.

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1 The observed inferior performance of the commercially available Pt/VC with respect to the ORR scans 2 revealed clearly their limitation in the currently available commercial Pt/VC catalyst for fuel cell 3 applications. The reference catalyst, Pt/TiO<sub>2</sub>, utilized in this work to PtPb/TiO<sub>2</sub> also showed the inferior 4 ORR performance in terms of the onset potential (0.43 V) compared to Pt/VC. The onset potential of 5 Pt/TiO<sub>2</sub> is shifted to a lower electric potential compared to Pt/VC by 130 mV. However, Pt/TiO<sub>2</sub> maintained the same onset potential (Figure 6a) and the current density (Figure 6b) even after 50 cycles, 6 7 indicating their stable ORR performance towards ORR. Interestingly, PtPb/TiO<sub>2</sub> showed the substantial stability as well as electrocatalytic activity towards ORR both in terms of the onset potential and the 8 9 current density, which are not changed significantly after 50 ORR cycles. PtPb/TiO<sub>2</sub> showed the higher onset potential shift of 180 mV and observed at 0. 61 V compared to Pt/TiO<sub>2</sub>. The enhanced and stable 10 performance of PtPb/TiO<sub>2</sub> compared to Pt/TiO<sub>2</sub> and the commercially available Pt/VC is due to the 11 changes in the electronic structure as evidenced from XPS results (see Figure 3 and corresponding 12 13 discussion) as well as their strong interaction with the TiO<sub>2</sub> support as evidenced from the TEM images (Figure 9b). The observed intriguing properties of PtPb/TiO<sub>2</sub> are promising to realize the practical 14 cathode catalyst towards ORR. Therefore, the dispersion of the PtPb NPs on the TiO<sub>2</sub> support through a 15 16 wet-chemical route may be an alternative catalyst to the commercially available Pt/VC catalyst both in 17 terms of the onset potential and the mass activity.

The stability of the catalytic centers under electric potential condition is crucial to realize long-18 19 term catalytic performance for fuel cell applications. Therefore, the influence of electric potential cycling over the electrodes of Pt/VC, Pt/TiO<sub>2</sub>, and PtPb/TiO<sub>2</sub> were examined by cycling of the 20 electrodes in Ar-saturated 0.1 M H<sub>2</sub>SO<sub>4</sub> solution at a scan rate of 50 mVs<sup>-1</sup>. The CVs of Pt/VC, Pt/TiO<sub>2</sub>, 21 and PtPb/TiO<sub>2</sub> for first, 100th, and 500th cycle are shown in the Figure 7. Figure 7*a* represents a series 22 of CVs obtained for Pt/VC, which shows the characteristic peaks for hydrogen adsorption/desorption (-23 0.2 to 0.1 V) as well as the formation of oxide moieties (0.5 to 1.2 V) and their corresponding reduction 24 25 (0.2 to 0.8 V). The intensities of these peaks, however, decreased significantly with increasing of the 26 electric potential cycling owing to the loss in the surface area of Pt on VC caused by the agglomeration 27 of the Pt NPs (see also Figure 8 and corresponding discussion) as the result of carbon corrosion and Pt dissolution through the Ostwald ripening during electric potential cycles.<sup>35-39</sup> It has also been proved 28 that the oxidation of carbon could be accelerated by the presence of Pt in the electrode materials.<sup>40-42</sup> 29 30 These results again stressed that there should be an essential need to find an alternative to the carbon

31 support to realize the stable and the long-term catalytic performance in fuel cells.



Figure 7. Cyclic voltammograms of  $1^{st}$  (solid line),  $100^{th}$  cycle (dotted line), and  $500^{th}$  cycle (dashed line) of Pt/VC (*a*), Pt/TiO<sub>2</sub> (*b*), and PtPb/TiO<sub>2</sub> (*c*) obtained in Ar-saturated 0.1 M H<sub>2</sub>SO<sub>4</sub> solution at a scan rate of 50 mVs<sup>-1</sup>. The proton adsorption/desorption peaks (highlighted area) for Pt/TiO<sub>2</sub> are shown in the insets (Figure 7*b*).

Figure 7*b* shows the CVs of Pt/TiO<sub>2</sub> in Ar-saturated 0.1 M H<sub>2</sub>SO<sub>4</sub> solution at a scan rate of 50 mVs<sup>-1</sup> for 500 cycles. The Pt/TiO<sub>2</sub> electrode also showed the similar characteristic hydrogen adsorption/desorption peaks in the region of -0.2 to 0.1 V and the formation of oxide moieties (0.36 V) and their corresponding reduction peaks (0.33 V), however, the intensities of these peaks increased with increasing of the electric potential cycling. The observed trends of Pt/TiO<sub>2</sub> are entirely different than that of the trends obtained from Pt/VC. The oxide moieties were formed during the oxidation reaction in the anodic scan, which are usually interacted on active Pt sites.<sup>8,9</sup> Therefore, the further oxidation reaction on the active Pt sites was hindered due to the blocking of active Pt sites by oxide moieties. However, the continuous electric potential cycling would likely remove the formed oxide moieties from the active Pt sites and thus the fresh active Pt sites can be generated for further reaction. Hence, the peak intensity for the formation of oxide moieties and their reduction increased with increasing of the electric potential cycling.

7 Figure 7c shows the CVs of PtPb/TiO<sub>2</sub> in Ar-saturated 0.1 M H<sub>2</sub>SO<sub>4</sub> solution at a scan rate of 50 mVs<sup>-1</sup>. PtPb/TiO<sub>2</sub> showed the characteristic peaks for the formation of oxide moieties and their 8 9 corresponding reduction at  $\sim 0.48$  V in the first cycle, however, no characteristic hydrogen adsorption/desorption peaks were observed. The peak intensities of the formation of oxide moieties and 10 their corresponding reduction are progressively decreased with increasing of the electric potential 11 cycling and no characteristic peaks were virtually observed at 500th cycle. The electric potential 12 13 cycling of PtPb/TiO<sub>2</sub> would most likely inhibit the formation of oxide moieties during anodic scan and therefore no corresponding reduction reaction on the PtPb surface. Thus, the PtPb/TiO<sub>2</sub> electrode 14 showed the intriguing difference compared to Pt/VC and Pt/TiO<sub>2</sub> in the formation of hydrogen 15 16 adsorption/desorption as well as oxide moieties/reduction due to the changes in the electronic structure of PtPb than Pt as evidenced from the XPS results (see the Figure 3). The similar trends were also 17 reported for TiO<sub>2</sub>-supported PtPd intermetallic systems.<sup>48</sup> Moreover, the ORR activity of PtPb/TiO<sub>2</sub> 18 was compared with the commercially available Pt/VC catalyst after 500 electric potential cycles, which 19 showed the stable ORR activity compared to Pt/VC (Figure S5). 20



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Figure 8. TEM images of the commercially available Pt/VC (20 wt.%) before (a) and after (b) electric
potential cycling. The size distribution of the Pt NPs on VC before (c) and after (d) electric potential
cycling is shown in the histograms.

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The influence of electric potential cycling on Pt/VC, Pt/TiO<sub>2</sub>, and PtPb/TiO<sub>2</sub> was further examined by observing of their morphologies after 500 electric potential cycles. Figure 8*a* shows the TEM image of Pt/VC before electric potential cycling. The Pt NPs observed as dark spots are finely dispersed on the carbon support as can be seen as light colored material. The particle size distribution of the Pt NPs on the carbon support before electric potential cycling is shown in the histogram (Figure 8*b*). The particle size showed the symmetrical distribution having the range between 1 and 5 nm centered at 3 nm (Figure 8*c*). However, the Pt NPs on the carbon support showed the remarkable increase after 500 electric potential cycles and showed the broad range distribution between 1 and 14 nm as shown in the histogram (Figure 8*d*). The increase in the particle size of Pt/VC is due to the agglomeration of the Pt particles through the Ostwald ripening after electric potential cycles.<sup>35-39</sup>



Figure 9. TEM image of Pt/TiO<sub>2</sub> (a) and PtPb/TiO<sub>2</sub> (b) after electric potential cycling of 500 cycles.
The size distribution of the Pt (c) and the PtPb (d) NPs on the TiO<sub>2</sub> support after electric potential
cycling is shown in the histograms.

Figure 9a shows the TEM image of Pt/TiO<sub>2</sub> after electric potential cycling of 500 cycles. The Pt 23 24 particles are again observed as dark colored spots on the TiO<sub>2</sub> support. Pt/TiO<sub>2</sub> also showed the symmetrical distribution having the range between 2 and 10 nm centered at 6 nm as shown in the 25 26 histogram (Figure 9c). However, the particle size of the Pt NPs increased nearly double in size after electric potential cycling compared to that of before electric potential cycling (see the Figures 2a and 27 28 2b). Although chemically as well as electrically resistant TiO<sub>2</sub>-support was utilized, however, the Pt 29 NPs were agglomerated after electric potential cycling on the TiO<sub>2</sub> support due to likely the weak 30 interactions between the Pt NPs and the TiO<sub>2</sub> support. It should be noted that the dispersivity of the Pt NPs on the carbon support was altered significantly before and after electric potential cycling (Figure 31 32 8), however, was not altered significantly in the case of Pt/TiO<sub>2</sub>. Figure 9b shows the TEM image of PtPb/TiO<sub>2</sub> after electric potential cycling of 500 cycles. Surprisingly, the particle size of the PtPb NPs 33

was greatly suppressed due to likely the strong interactions between the PtPb NPs and the TiO<sub>2</sub> support.

as well as their dispersion on the TiO<sub>2</sub> support was not changed significantly even after electric
potential cycling of 500 cycles. The particle size shows the symmetrical distribution and having the
range between 1 and 6 nm centered at 3 nm after electric potential cycling of 500 cycles (Figure 9*d*),
which is virtually same with the particle size of the PtPb NPs on the TiO<sub>2</sub> support before electric
potential cycling (see the Figures 2*c* and 2*d*). The agglomeration of the PtPb NPs on the TiO<sub>2</sub> support

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#### 8 Conclusion

9 Finely dispersed, intermetallic PtPb NPs with an average particle size of 3 nm on anatase TiO<sub>2</sub> were prepared by co-reduction of Pt- and Pb precursors through a wet-chemical synthesis route. The 10 formation of intermetallic phase between Pt and Pb on the TiO<sub>2</sub> support was confirmed by pXRD and 11 XPS experiments. The reference catalyst, Pt/TiO<sub>2</sub> with the similar particle size of 3 nm to PtPb/TiO<sub>2</sub> 12 13 was also prepared to compare the catalytic activity. PtPb/TiO<sub>2</sub> showed a seven-times higher ORR mass activity and a substantial shift (180 mV) in the onset potential towards a higher electric potential 14 15 compared to Pt/TiO<sub>2</sub>. PtPb/TiO<sub>2</sub> also showed the long-term and stable ORR performance compared to the commercially available Pt/VC (Pt loading: 20 wt.%). The dispersivity and the particle size of the 16 17 PtPb NPs on the TiO<sub>2</sub> support were not altered significantly after electric potential cycling of 500 cycles in an aqueous solution of 0.1 M H<sub>2</sub>SO<sub>4</sub> due to the strong interactions between the PtPb NPs and 18 the TiO<sub>2</sub> support. Conversely, the Pt NPs were agglomerated significantly both in the case of Pt/TiO<sub>2</sub> as 19 well as the commercially available Pt/VC after 500 cycles due to the weak interactions between the Pt 20 21 NPs and the supports (TiO<sub>2</sub> or VC). The observed superior performance of PtPb/TiO<sub>2</sub> is due to the 22 changes in the electronic structure of Pt in the PtPb NPs compared to the Pt NPs as well as their strong 23 interactions with the TiO<sub>2</sub> support. PtPb/TiO<sub>2</sub> can be utilized as cathode electrode catalysts for direct 24 fuel cell applications.

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Supplementary Information available: [Bright-field TEM images of Pt and PtPb NPs; XPS profile
for PtPb/TiO<sub>2</sub> in the C 1s region; Cyclic voltammograms of Pt NPs, PtPb NPs, Pt/VC, Pt/TiO<sub>2</sub>, and
PtPb/TiO<sub>2</sub> in argon and oxygen saturated 0.1 M H<sub>2</sub>SO<sub>4</sub>; ORR performance of Pt/VC (10 wt.% and 20
wt.%) and PtPb/TiO<sub>2</sub> after 500 electric potential pre-treatment; *p*XRD profile for Pt/VC; Comparison
of ORR of Pt/TiO<sub>2</sub>, PtPb/TiO<sub>2</sub>, and Pt/VC; XPS profile for Pt/TiO<sub>2</sub> and PtPb NPs; ICP-MS analysis]

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Anatase-type titania supported intermetallic PtPb nanoparticles synthesized through wet-chemical route showed long-term, stable, and improved oxygen reduction reaction performance