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7 **Stability and Activity of Pt/ITO Electrocatalyst for Oxygen Reduction**
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9 **Reaction in Alkaline Media**
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ABSTRACT

Because of the activity for carbon materials to rapidly form peroxide-like species in alkaline media which cause considerable membrane degradation, there is a significant need to find stable non-carbon support material for Pt and other oxygen reduction reaction (ORR) catalysts. The objective of this study was to investigate the performance of platinum supported on tin-doped indium oxides (ITO) electrocatalysts for the ORR in alkaline media. Platinum was deposited onto ITO by galvanic displacement and the Pt/ITO was physically characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). Electrochemical experiments showed that Pt/ITO catalysts outperform commercial Pt/Vulcan in terms of both activity and stability. The specific activity and mass activity of Pt/ITO were about 2.5 times that of Pt/Vulcan. After 300 potentiometric cycles in O₂-saturated alkaline electrolyte, only 17.4% loss in the electrochemical surface area (ECSA) was observed for Pt/ITO, which compares favorably to Pt/Vulcan at 37.5%. The good durability of Pt/ITO at a relatively high specific activity provides one of the first examples of successful deployment of a non-carbon support for anion exchange membrane fuel cell catalysts.

KEYWORDS: *Oxygen reduction; Platinum; Tin-doped indium oxide; Alkaline media; Electrocatalyst.*

1. INTRODUCTION

The study of electrocatalyst activity and stability in alkaline media was a popular research topic from the 1960s through the 1980s because of the development of alkaline fuel cells (AFCs) for space applications¹. However its terrestrial development was limited by problems with electrolyte carbonation and electrolyte leakage. Recent designs of AFCs such as laminar flow-based micro fuel cell and the breakthrough development of stable, high conductivity anion exchange membranes and ionomers have started to overcome the problems of conventional AFCs and revive researchers' interest in electrochemical reactions in alkaline media²⁻⁴.

The oxygen reduction reaction (ORR), which occurs at the AFC and anion exchange membrane fuel cell (AEMFC) cathode, is one of the most widely studied reactions to date. Though the shift in potential with pH is very well known (0.059V/pH) and often discussed, the differences in the interface and its role in the ORR mechanism are not as well known. First, the lower potential required for the ORR in alkaline media changes the surface free energy, weakening the Pt-O bond energy compared to acid electrolyte⁵. This decreased bond energy, combined with the outer-sphere electron transfer mechanism^{6, 7} decreases the overpotential for the ORR in alkaline media relative to acidic media. Simply put, the ORR in alkaline media is more facile than it is in acid and catalytic activity has been observed over much of the periodic table from carbon compounds⁸⁻¹⁰, to various transition metals¹¹⁻¹³, coinage metals¹⁴⁻¹⁷, metal macrocycles including porphyrins^{18, 19}, phthalocyanines^{20, 21} and metal oxides²². Although some high activity non-platinum group metal catalysts have been shown for the ORR in alkaline media^{23,24}, Pt-based catalysts still remain one of the most popular in the literature because of their

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5 proven combination of high stability and activity. However, the properties of the ORR
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7 suggest that even lower Pt loading are possible in alkaline media, leading to lower overall
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12 Another method to decrease the Pt loading is to use alternative support materials to
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14 carbon that are able to manipulate the Pt dispersion, size, shape, etc. through electron
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16 transfer between the catalyst and support. Finding alternative supports to carbon is also a
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18 pressing issue in alkaline media because of the high activity of carbon towards the two-
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20 electron reduction of oxygen to hydrogen peroxide²⁵. The role of peroxide-induced
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22 membrane degradation is well documented in both acid and alkaline media⁴. Among the
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24 state-of-the-art support materials, metal oxide supports as alternatives to carbon have
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26 generally shown improved corrosion resistance and reduced electrochemical surface area
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28 (ECSA) degradation rates²⁶⁻³². Metal-support interactions can also improve the
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30 electrocatalytic activity of the supported Pt in several ways such as modification of the
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32 electronic states of Pt to increase the potential of the formation of Pt-OH groups³³ and
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34 reduction of the equilibrium OH adsorption by lateral repulsion between Pt-OH and oxide
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36 surface³⁴⁻³⁶. Recent study on ITO nanoparticles (NPs) as a high stability non-carbon
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38 support for Pt NPs³⁷ showed that the mass activity of Pt/ITO for the ORR in acidic media
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40 was considerably higher than that of the 2017 DOE goal³⁸, which may be due in part to
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42 epitaxial Pt orientation dictated by the metal oxide surface. The ITO support material also
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44 demonstrated great stability, even in a harsh acidic and oxidizing environment. This
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46 result further supported previous work that the strong interaction between Sn and Pt
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48 suppresses the formation of Pt-oxide species at high potentials to provide a clean surface
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50 over a wide potential range and is beneficial for the stability of Pt³⁹. Therefore, metal
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oxides, as the support materials, can provide modifications for Pt to increase the electrocatalytic activity and stability.

In this study, the application of ITO as an electrocatalyst support for Pt in alkaline media was explored. The ORR activity and stability of Pt/ITO were compared with a commercial Pt/Vulcan electrocatalyst. The differences of Pt/ITO catalyst in acidic and alkaline media, and the possible reasons for its high activity and stability were discussed.

2. EXPERIMENTAL SECTION

2.1 *Synthesis of ITO supports*

To prepare the ITO nanoparticles (NPs), a slurry of indium acetylacetonate ($\text{In}(\text{acac})_3$) (99.99+%, Sigma-Aldrich) and tin bis-(acetylacetonate) dichloride ($\text{Sn}(\text{acac})_2\text{Cl}_2$) (98%, Sigma-Aldrich) precursors was prepared in oleylamine (70%, Sigma-Aldrich) (4 ml). The ratio of In to Sn atoms was 19:1 (14.11 mg of tin bis-(acetylacetonate) dichloride was used). Then the slurry was heated at 200 °C for 1.5 hours in air to produce a dark yellow suspension. The ITO nanoparticles (NPs) were precipitated by the addition of ethanol (40 ml) to the suspension, and the supernatant was removed by centrifugation at 2500 RPM (revolutions per minute) for 6 min. After washing with ethanol again, white ITO NPs were yielded. They were heated at 80 °C for 0.5 hours to evaporate remaining ethanol and then further heated at 500 °C for 2 hours in air for crystallization.

2.2 *Deposition of Pt on ITO*

The first step was to disperse the as-synthesized ITO onto a mirror-polished 5 mm-

diameter glassy carbon electrode (GCE) (Pine Research Instrumentation). The GCE was polished to a mirror finish using a 0.05 μm alumina-particle suspension (Buehler) on a moistened polishing microcloth (Buehler) and washed ultrasonically with ultra-pure 18.2 M Ω deionized water (from a Millipore Direct-Q 3UV purification system) for 4 min prior to each experiment. The ITO/water dispersion was prepared (0.1 mg/ml ITO) by sonication for 30 minutes, forming an opaque and uniform suspension. 20 μl of the suspension was added dropwise onto the GCE with a micropipet and then dried in air for 60 min on an inverted rotating disk electrode (RDE) at 300 RPM (Pine Research Instrumentation). A homogeneous light gray thin film was obtained on top of the GCE. The loading of ITO NPs on the working electrode was approximately 10.2 $\mu\text{g cm}^{-2}$.

The procedure for Pt deposition onto the ITO supports was by galvanic displacement of a Cu monolayer. Cu coverage was carried out in a custom-built three-electrode electrochemical cell (Adams & Chittenden Scientific Glass) in N_2 atmosphere to avoid Cu oxidation. Cu was electrodeposited by cyclic voltammetry (CV) (Autolab PGSTAT302N Potentiostat, Eco Chemie) without rotation in a 0.05 M H_2SO_4 /0.05 M CuSO_4 solution between 0.0 and 0.3 V vs. normal hydrogen electrode (NHE) for two cycles at a sweep rate of 50mV/s. All potentials are reported versus NHE. The resulting electrode was rinsed with copious Millipore water, transferred to a dilute, deaerated 0.001 M K_2PtCl_4 (Acros Organics)/0.05 M H_2SO_4 solution and was kept there for 5 minutes at room temperature, which facilitated the galvanic displacement of Cu by Pt⁴⁰. Then the electrode was rinsed with copious Millipore water again. At last, a thin layer of Nafion[®] diluted to 0.05wt% from 5% Nafion[®] DE-520, DuPont was pipetted onto the working electrode in order to attach the supporting material to the GCE during electrochemical

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5 reaction. The Nafion[®] film was dried under 300 RPM in air at room temperature. The
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7 loading of Pt onto ITO was 6.3 $\mu\text{g cm}^{-2}$ (by calculating the charge difference during the
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9 anodic and cathodic scan³⁷).
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14 2.3 Physical Characterization of ITO and Platinized ITO.

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17 The crystal structure and average grain boundary size in the ITO electrocatalyst
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19 support were evaluated by Bruker D8 Advance X-ray diffractometer with a Cu K α_1
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21 ceramic X-ray tube ($\lambda = 0.1540562$ nm) and a LynxEye Super Speed detector. The
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23 diffraction angle (2θ) was varied from 5° to 90° at a scanrate of 0.0285°/second. The
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25 morphology and nanostructure of the support was investigated by transmission electron
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27 microscope (TEM) with a Tecnai T-12 and a FasTEM JEOL 2010. X-ray photoelectron
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29 spectroscopy (XPS) was performed using a Physical Electronics multiprobe with a
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31 Perkin–Elmer dual anode X-ray source and a Kratos AXIS-165 surface analysis system to
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33 investigate the surface composition of the as-synthesized support material and the
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35 composition change after durability test.
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44 2.4 Electrochemical Characterization of ITO and Pt/ITO.

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46 Electrochemical experiments were carried out in a three-electrode electrochemical cell
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48 with a water jacket. CVs and polarization curves for the oxygen reduction reaction were
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50 recorded at 25°C (thermostated by Isotemp 3016D, Fisher) using an Ecochemie Autolab
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52 PGSTAT302N potentiostat. A Pt flag and a saturated calomel electrode (CH Instruments)
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54 were used as counter and reference electrodes, respectively. The electrolytes used in the
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56 electrochemical tests included 0.1 M perchloric acid (HClO₄) (70%, Acros Organics) and
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0.1 M potassium hydroxide (KOH) solution made from KOH pellets ($\geq 85.0\%$ Certified ACS, Fisher Chemical). And both the electrolytes were deaerated by bubbling with UHP grade nitrogen (Airgas) for 45 minutes before CV tests and saturated with O₂ by bubbling with USP grade oxygen (Airgas) for 45 minutes before conducting the polarization curves. Before every electrochemical test, each as-prepared electrode was kept under 40 cycles of cleaning sweeps between 0 to 1.4 V in N₂-saturated electrolyte at 200 mV/s (break-in cycles).

3. RESULTS AND DISCUSSION

3.1 Evaluation of Crystal Structure Using XRD.

Powder XRD pattern of the as-synthesized support material composed of ITO NPs with phase identification is shown in Figure 1. Five major peaks and three minor peaks were observed between the 20° and 65° diffraction angle (2 θ) located at 21.32° (211), 30.60° (222), 35.45° (400), 37.51° (411), 41.74° (332), 45.54° (431), 50.96° (440) and 60.55° (622).

Figure 1. Powder XRD patterns for pure ITO crystals with 5 atom % of Sn content.

The observed pattern corresponded well with a bixbyite In₂O₃ cubic structure (JCPDS 06-0416) with no secondary phases showing that elements tin and indium did not exist as segregated solid oxides, rather tin existing as a dopant into the indium oxide lattice. The average grain boundary size for the ITO NPs was calculated from the Scherrer equation, Eq. (1):

$$D = \frac{k\lambda}{B\cos\theta} \quad (1)$$

where D is the grain boundary size (nm), k is the shape factor (taken as 0.89), λ is the X-ray wavelength (nm), B is the width (radians) at half the maximum peak intensity, and θ is the Bragg angle. The average side length for the cubic ITO NPs was 26.74 nm.

3.2 Nanostructure of As-Synthesized ITO Electrocatalyst Supports and Platinized ITO.

The representative morphologic features of the as-prepared metal oxides were examined by transmission electron microscopy (TEM), shown in Figure 2a. The support ITO NPs exhibited a cubic-like shape with a mean particle size around 22 nm (side length), which were evaluated from an ensemble of approximately 50 particles in arbitrary areas of the corresponding TEM images, such as Figure 2a (size and distribution of ITO NPs shown in Figure S1c). The high-resolution TEM images in Figure 2b show a well-crystallized lattice structure with a highly ordered continuous fringe pattern. The size of Pt NPs supported on ITO was around 5 nm (typical value) in diameter, as can be observed from the small darkly contrasting spherical Pt NPs dispersed on the supports in Figure 2c.

Figure 2. (a) TEM images of ITO NPs; (b) high-resolution TEM images of ITO NPs; (c) Pt NP supported on ITO.

3.3 Surface Characterizations of Prepared ITO Support and Pt/ITO.

The surface compositions of ITO and Pt/ITO were examined by XPS. The activity and stability of electrocatalysts can be evaluated by the surface composition. Changes that occur during operation can provide critical information about what happens to the

electrocatalyst in the reaction environment. Figure 3 shows the broad XPS survey (a), focused C 1s (from carbon tape) (b), focused In 3d (c) and focused Sn 3d (d) spectra of the as-synthesized ITO NPs. In the survey spectra, with binding energy from 1100 to 0 eV, all of the expected elements were observed: fluorine (Nafion[®]), oxygen, tin, indium, and carbon (substrate). The relative atomic percentage of tin was about 14%, almost three times that of the bulk, which could be caused by Sn surface segregation in the ITO structure⁴¹.

The binding energies for all of the elements were referenced to the C 1s main peak. As shown in Figure 3b, there was a small satellite peak on the higher binding energy side of the C 1s main peak suggesting there were more than one types of carbon on the sample holder. Six different peaks were fitted to the main and satellite peaks to get the closest value of full width at half maximum (FWHM), which is 1.8 for graphite carbon. Therefore the peak with the largest area was chosen as the calibration reference.

Figure 3. (a) XPS survey spectra of the as-synthesized ITO NPs; (b) focused C 1s spectra of ITO NPs supported on carbon tape; (c) focused In 3d spectra of the as-synthesized ITO NPs; (d) focused Sn 3d spectra of the as-synthesized ITO NPs.

The high-resolution spectra for In 3d in Figure 3c could only be deconvoluted into one doublet at 444.37 eV and 451.91 eV. They corresponded with the binding energy of In³⁺ 3d_{5/2} and In³⁺ 3d_{3/2}. However, the high-resolution spectra for Sn 3d was deconvoluted into two doublets (four peaks). The generally accepted value for the deconvoluted peaks of Sn⁴⁺ 3d_{5/2} and Sn²⁺ 3d_{5/2} are 487.1 eV and 486.1 eV, respectively, which can be used to distinguish Sn⁴⁺ and Sn²⁺ states and their relative concentrations on the ITO surface as

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5 shown in Figure 3d. The binding energies of the first deconvoluted doublet peaks labeled
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7 by blue lines corresponded to the $\text{Sn}^{4+} 3d_{5/2}$ and $\text{Sn}^{4+} 3d_{3/2}$. The second doublet peaks
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9 labeled in red lines in the lower binding energy area were consistent with $\text{Sn}^{2+} 3d_{5/2}$ and
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11 $\text{Sn}^{2+} 3d_{3/2}$. 96.5 atom % of Sn in the as-prepared ITO support existed in the Sn^{4+} state
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13 with the balance being Sn^{2+} .
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17 The surface compositions of fresh Pt/ITO and Pt/ITO after 40 break-in cycles in N_2 -
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19 saturated HClO_4 electrolyte were also investigated by XPS. From the survey spectra of
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21 Pt/ITO shown in Figure 4a, Pt 4f peak was also observed in addition to the expected
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23 elements from ITO.
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29 **Figure 4.** (a) XPS survey spectra of the Pt/ITO; (b) focused Sn 3d spectra of fresh Pt/ITO; (c) focused Sn
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31 3d spectra of Pt/ITO after 40 cycles of breaking in; (d) focused In 3d spectra of Pt/ITO.
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35 The high-resolution spectra for Sn 3d was again deconvoluted into two doublets for
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37 Sn^{4+} and Sn^{2+} states, with the difference that the percentage of Sn^{2+} state on the surface
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39 increased from 3.5% (fresh ITO in Figure 3d) to 9% (as-deposited Pt/ITO in Figure 4b)
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41 and then to 20% (Pt/ITO after break-in cycles in Figure 4c). Both the electrochemical
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43 deposition of Pt onto the ITO NPs and the protonated break-in cycling in the electrolyte
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45 played a role in the reduction of the surface Sn. It is known that the tin atoms at the
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47 interface with Pt can be reduced by a Schottky junction formed by aligning Fermi levels⁴².
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49 Another significant difference was that after referencing to C 1s main peak for all the
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51 XPS samples, the positions of the Sn peaks and In peaks for Pt/ITO shifted negatively by
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53 around 0.3 eV compared to those in pure ITO NPs. This may support the existence of a
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strong metal-support interaction between Pt and ITO, which may result in electron transfer between Pt and surface Sn, impacting activity and stability of Pt/ITO.

3.4 CVs and ECSA of Pt/ITO in alkaline media

CV of Pt/ITO in N₂-saturated 0.1 M KOH solution at 25°C is shown in black in Figure 5 after positively shifting the working potential range by 0.708V ($E_{\text{shifted}} = 0.059\text{V/pH}^* (13_{\text{pH}} - 1_{\text{pH}}) = 0.708 \text{ V}$) in order to be consistent with activity studies in acidic media. The shifted CV showed two distinct potential regions. The specific adsorption of hydroxide anions and Pt oxidation was observed above 0 V⁴³⁻⁴⁵. Hydrogen adsorption/desorption processes between $-0.7 < E < -0.35 \text{ V}$, caused by proton transfer from water molecules co-adsorbed on the electrode surface in alkaline media. This explains why the hydrogen adsorption/desorption peaks were much smaller than that in acidic solution, which can be clearly observed in the comparison in Figure 5. It also explains why the double layer region is not as wide in alkaline vs. acid media⁴⁵⁻⁴⁷.

Figure 5. Pt/ITO CV comparison in acidic and alkaline media (CV in KOH was shifted by ~0.7 V).

On account of the more complex interaction in alkaline media, electrochemically active surface area (ECSA) determination is nearly always performed by hydrogen adsorption in acid media. The ECSA is determined by integrating the hydrogen adsorption charge (Q_{r}) in the negative-going underpotential scan (0.40-0.075 V) in N₂-saturated 0.1 M HClO₄ electrolyte (Figure 4) after correction for double-layer charges⁴⁸. As shown in Equation 2,

$$ECSA = \frac{Q_r}{m \times C} \quad (2)$$

Where m is the mass of Pt loading, Q_r is the H_2 underpotential adsorption charge, C is the charge of full coverage of monolayer for clean polycrystalline Pt ($210 \mu C \text{ cm}^{-2}$). The Pt/ITO ECSA in this work was $74.4 \text{ m}^2/\text{g}_{Pt}$, almost three times that of Pt/Vulcan ($27.3 \text{ m}^2/\text{g}_{Pt}$).

3.5 ORR activity of Pt/ITO in alkaline media

The oxygen reduction activity of Pt/ITO in alkaline media was studied by anodic linear sweep voltammograms and compared to that of Pt/Vulcan in alkaline media. The ORR measurements for both Pt/ITO and Pt/Vulcan rotating-disk electrodes (RDEs) were performed in O_2 -saturated 0.1 M KOH at a scanrate of 10 mV/s from 400 RPM to 2500 RPM , which was repeated five times to ensure reproducibility. The Pt/ITO loading was approximately $16.5 \mu\text{g cm}^{-2}$ (the total loading of Pt and ITO NPs), whereas the loading was approximately $27.6 \mu\text{g cm}^{-2}$ for Pt/Vulcan. From the comparison of the 1600-RPM polarization curves (Figure 6a) of Pt/ITO and Pt/Vulcan, the half-wave potential of Pt/ITO was 17 mV more positive than that of Pt/Vulcan.

The ORR kinetics analysis was carried out by Koutecky-Levich analysis of the background-corrected (by subtracting background current measured under identical conditions under N_2 atmosphere without rotation) and IR-corrected (by subtracting the current multiplied by the solution resistance) polarization curves. A well-developed diffusion limited current density plateau for Pt/ITO, $J_{lim} (\sim 5.2 \text{ mA cm}^{-2})$, was observed from -0.7 V to -0.1 V . J_{lim} was within the 10% margin of the theoretical diffusion limiting current calculated from Levich Equation ($J_{lim} = 0.62nFD_i^{2/3}v^{-1/6}C_o^*w^{1/2} = 5.66$

mA cm⁻²), followed by the mixed kinetic-diffusion control region -0.1 V < E < 0.1 V.

Therefore the kinetic current (I_k) was obtained by Equation 3⁴⁹:

$$I_k(A) = \frac{I_{lim}(A) \times I(A)}{(I_{lim} - I)} \quad (3)$$

Then the specific activity of Pt/ITO catalyst (calculated from the 1600-RPM polarization curve) in KOH electrolyte was calculated by normalizing I_k to the Pt electrochemical surface area according to Equation 4⁴⁹:

$$I_s(\mu A cm_{Pt}^{-2}) = \frac{I_k(A)}{Q_{H-adsorption}(C)/210 \mu C cm_{Pt}^{-2}} \quad (4)$$

Which was 0.326 ± 0.04 mA cm⁻² at 0.1 V, 2.65 times of that of Pt/Vulcan (0.123 ± 0.01 mA cm⁻²). Our experimental value of the specific activity of Pt/Vulcan was comparable to the activity of synthesized Pt/Vulcan (0.120 mA cm⁻²) previously reported⁵⁰. The mass activity of Pt/ITO catalyst in KOH was obtained by normalizing I_s to the loading amount of Pt metal. The mass activity for Pt/ITO catalyst (243 mA/mg_{Pt}) was about 1.47 times greater than that of Pt/Vulcan (98.3 mA/mg_{Pt}) in alkaline media, and much higher than the previously reported (60 mA/mg_{Pt})⁵⁰.

From -0.4V to 0.05V, linear Koutecky–Levich plots of both Pt/ITO (Figure 6c) and Pt/Vulcan (Figure S2b) were observed (assuming both first order kinetics), plotting J^{-1} vs. $\omega^{-1/2}$ 51.

$$\frac{1}{J} = \frac{1}{J_k} + \frac{1}{J_{diff}} = \frac{1}{J_k} + \frac{1}{B\omega^{1/2}} \quad (5)$$

$$B = 0.62nFC_0D_0^{2/3}\eta^{-1/6} \quad (6)$$

where J_k and J_{diff} are the kinetic and diffusion limited current densities respectively, F is the Faraday constant, C_0 is the saturated concentration of O₂ in the 0.1 M KOH electrolyte (1.21×10^{-3} mol/L), D_0 is the diffusion coefficient of O₂ in the KOH

electrolyte ($1.86 \times 10^{-5} \text{ cm}^2 \text{ s}$), and η is the viscosity of the electrolyte ($1.008 \times 10^{-2} \text{ cm}^2 \text{ s}$)⁵¹. From the slopes ($1/B$) of the Koutecky-Levich plots at different potentials between -0.4V to 0.05V, the average number of electrons, n , involved in the ORR in alkaline media can be obtained. Over the entire potential range, it was found that for Pt/ITO, $n \approx 4$ and for Pt/Vulcan, $n \approx 3.54$, which indicated that Pt/Vulcan can be more active in alkaline media to produce peroxide-like intermediates in the ORR mechanism than Pt/ITO.

Figure 6. (a) Comparison of the ORR polarization curves in alkaline media under 1600 RPM of Pt/ITO and Pt/Vulcan; (b) room temperature rotating disk voltammograms of Pt/ITO electrocatalyst in O_2 -saturated 0.1 M KOH, scanrate, 10 mV/s; (c) Koutecky–Levich plots (J^{-1} vs. $\omega^{-0.5}$) of Pt/ITO at different potentials; (d) Tafel plot of Pt/ITO derived by the mass-transport-corrected 1600 RPM polarization curve.

Figure 6d shows the Tafel plot for the ORR on Pt/ITO in KOH electrolyte at 1600 RPM. It shows two clearly discerned Tafel regions, which are 0.05 V to 0.15 V and 0.15 V to 0.2 V, with corresponding slopes of 129 mV/dec and 69 mV/dec, respectively. They attributed to the formation and adsorption of surface oxides on the Pt surface. This is consistent with the literature data on supported polycrystalline Pt nanoparticles⁵⁰.

3.6 Electrochemical Stability of Raw and Platinized ITO Supports.

Though ITO crystals have shown good bulk chemical stability in acid and alkaline media, previous studies have shown that the ITO surface composition can change significantly during electrochemical treatment, particularly at elevated potentials^{53, 54}. CVs of raw ITO supports in both O_2 -saturated and N_2 -saturated 0.1 M KOH (Figure S3a and S3c) were collected at room temperature without rotation to determine the intrinsic

redox stability of ITO in the potential window relevant to the ORR. For all curves in the oxygenated alkaline electrolyte, there were no obvious redox peaks, and ITO only showed typical capacitive behavior.

The stability was investigated by cycling the potential of Pt/ITO between -0.2 and 0.4 V for 300 cycles at 10 mV/s without rotation in O₂-saturated 0.1 M KOH electrolyte (Figure S3b). There was a slight decrease in both the ECSA (Figure 7a) and the current density for the reduction of Pt-O. After 300 cycles, the ECSA (Figure 7a) decrease was approximately 17.4%, less than half of the 37.5% decrease found for the commercial Pt/Vulcan electrocatalyst (Figure 7b). After 300 cycles, the ORR half-wave potential shifted negatively by 20mV, the specific activity was decreased from $0.326 \pm 0.04 \text{ mA cm}^{-2}$ to $0.291 \pm 0.001 \text{ mA cm}^{-2}$ (Figure 7c), which compared favorably to both the shift in the half-wave potential (50mV) and specific activity of Pt/Vulcan.

The stability of Pt/Vulcan was also explored under the same conditions as Pt/ITO. But the half-wave potential shift of Pt/Vulcan was 50mV (Figure 7d), which means the performance stability of Pt/ITO catalyst for ORR in alkaline media was improved compared to Pt/Vulcan.

Figure 7. (a) CV comparison of Pt/ITO between -0.7 V and 0.7 V of before and after 300 cycles, in oxygen-saturated electrolyte; (b) CV comparison of Pt/Vulcan before and after 300 cycles, in nitrogen-saturated electrolyte; (c) ORR polarization curve comparison before and after 300 cycles on Pt/ITO catalysts on RDE. Sweep rate, 10 mV/s; rotating rate, 1600 RPM, (Pt loading: $6.3 \mu\text{g cm}^{-2}$); (d) ORR polarization curve comparison before and after 300 cycles on Pt/Vulcan catalysts on RDE. Sweep rate, 10 mV/s; rotating rate, 1600 RPM, (Pt loading: $17.3 \mu\text{g cm}^{-2}$).

The surface composition change was investigated by XPS (Figure 8). In the XPS spectra, surface In existed only as In_2O_3 showing no other state even after 300 cycles (Figure 8a). However, the percentage of Sn^{2+} on the surface increased from 20% before electrochemical reaction to 87% after 300 cycles (Figure 8b). Although the surface Sn^{4+} was gradually reduced to Sn^{2+} state during the stability cycling (Figure 8c), the specific activity of Pt/ITO after stability test was still 2.77 times that of commercial Pt after its stability test.

Figure 8. (a) In spectra in Pt/ITO after durability test; (b) Sn spectra in Pt/ITO after durability test; (c) surface composition differences between fresh ITO, fresh Pt/ITO, Pt/ITO before (after breaking in cycles) and after 300 cycles of reaction.

4. CONCLUSION

5% ITO was prepared as the support material for monolayer Pt and the electrocatalytic performance of Pt/ITO was evaluated for the ORR in alkaline environment. It was found that the mass activity and specific activity of Pt in Pt/ITO were nearly 2.5 times that of Pt/Vulcan in alkaline media, respectively. What's more, the stability of Pt/ITO electrocatalyst was also greater than that of Pt/Vulcan after a 300-cycle stability test between -0.2-0.4V in O_2 -saturated alkaline electrolyte. The ECSA loss in Pt/ITO was only less than half of that in Pt/Vulcan. The Pt/ITO electrocatalyst could maintained a high activity for ORR despite progressively reduced (Sn) surface during potentiometric cycling, which raises further discussion of the Pt-support interaction mechanism for oxygen reduction reaction in alkaline media, which will be investigated in our future

work. The purposeful utilization of Pt-support interactions may lead to promising new catalysts for the ORR and many other reactions of commercial interest.

5. ACKNOWLEDGMENTS

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