Exploring the Activity and Stability Limits for Pt/ITO ORR Electro catalysts

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Applications in Energy Conversion – Oxygen Reduction Reaction (ORR)

Anode: $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$

Cathode: $\frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$

Cell: $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$

Source: http://physics.nist.gov


Issues with Carbon Supported Pt

Non-Functionalized Graphitic Carbon
Limitations of State-of-the-Art Carbon Supports

- Catalyst Stability
- Carbon Corrosion

\[ C + H_2O \rightarrow C-O_{ad} + 2H^+ + 2e^- \]
\[ E^0 = 0.207\text{V} \]

\[ C-O_{ad} + H_2O \rightarrow CO_2 + 2H^+ + 2e^- \]
Catalyst Activity and Stability

- **Particle Size**
  - As size $\uparrow$, specific and mass Activity $\downarrow$
- **Particle Shape**
  - $\text{Pt}\{100\} \ll \text{Pt } \{111\} < \text{Pt } \{110\}$
- **Support**
  - Necessary
  - Carbon black not good enough
- **Non-inert supports?**

Key Questions for Design and Implementation of Non-Inert Supports

- Is it possible to increase the intrinsic activity of Pt nanoparticles by using the catalyst support. If so, what are the underlying mechanisms?

- Is it possible to make electrocatalyst supports that have better stability than graphitized carbon? How much would a material like that cost?

- Is it possible to increase the Pt nanoparticle stability by using the electrocatalyst support. If so, what are the underlying mechanisms? What support microstructure will optimize Pt utilization?
What to do?

- Design next-generation supports that interact more strongly with Pt*

Pt “anchor” improves nanoparticle stability

Increase Activity and Stability of Supported Pt

Control Pt electronic structure and shape

Promises and Limitations of SnO₂ as an Electrocatalyst Support

- Pt is well dispersed on SnO₂
- SnO₂ suppresses formation of Pt oxides
- Strong Interaction between Pt and Sn
- “New” redox couple

Promises and Limitations of SnO$_2$ as an Electrocatalyst Support

- In$_2$O$_3$ is stable in the ORR environment
- Pt/In$_2$O$_3$ doesn’t show significant ORR activity
- In$_2$O$_3$ --- semiconductor

ITO (Tin-doped Indium Oxide): Sn can be introduced into the $\text{In}_2\text{O}_3$ lattice electronic conductivity at 25°C ~ 0.1 S/cm

The ideal metal oxide surface:

- Conduction band
- Forbidden energy gap
- Valence band

The doped metal oxide surface contain oxygen vacancies and dopant sites.

The introduction of dopants can:
- Increase conductivity
- Form the Sn-rich shell structure, ensure the stability of the supports

Synthesis of 5% Sn-doped Indium Oxide (ITO) Supports

$\text{In}(\text{OCCH}_3\text{CHOCH}_3)_3 + \text{SnCl}_2(\text{OCCH}_3\text{CHOCH}_3)_2 \xrightarrow{\text{oleylamine}}$  

$\xrightarrow{200\degree C\, 1.5\text{h}} \xrightarrow{\text{diluted, precipitated, ethanol}} \xrightarrow{\text{centrifuged}} \xrightarrow{\text{washed, ethonal DI water}} \xrightarrow{\text{amorphous ITO}} \xrightarrow{500\degree C} \text{Crystalline ITO nanoparticles}$

Most of the exposed ITO crystal facets are $\{222\}$

Platinization of the ITO Supports

Galvanic displacement (ITO: 5 at% Sn, 500 °C)

A → B:
The deposition of Cu from CuSO₄, H₂SO₄ solution

B → E:
Rinsed to remove Cu²⁺ and placed into K₂PtCl₄, H₂SO₄ solution in an N₂ atmosphere

4-min immersion to replace Cu by Pt

20 wt% Pt/ITO
Pt nanoparticles have the average size of ~3 nm, dispersed well on the ITO.
Continuous lattice fringes from ITO with preferential \{111\} faceting.

ORR activity on Pt:
\[
\text{Pt}(100) \ll \text{Pt}(111) < \text{Pt}(110)
\]

ORR Activity of 20 wt % Pt/ITO

DOE 2017 Targets:
Specific Activity: 0.72 mA/cm²
Mass Activity: 0.44 mA/µg Pt

Electrochemical Stability of Pt/ITO for the ORR

Stability of Pt/Vulcan XC-72R ORR Electrocatalysts

![Graphs showing the stability of Pt/Vulcan XC-72R ORR Electrocatalysts before and after 1,000 cycles.](Image)
TEM, Figure (a)
- Small holes appeared on the ITO surface
- Corrosion of surface Sn

XPS, Figures (b-d)
- In existed only as \( \text{In}_2\text{O}_3 \) even after 1,000 cycles
- Percentage of \( \text{Sn}^{4+} \) reduced to 28% (from 91%) after 1,000 cycles between 0.0 and 1.4 V vs. NHE

Stability of Pt/Sn-In$_2$O$_3$ under ORR-relevant potentials (0.6≤E≤1.4)

Before Cycling

After Cycling
Load Cycling for Pt/ITO to Determine the Pt Stability

(a) Pt dissolution protocol; (b) Cyclic voltamograms of Pt/ITO with 3 cycle Pt deposition before and after 5000 cycles in an O_2-saturated 0.1 M HClO_4 solution recorded at 60 °C. Sweep rate: 50 mV/s.
How does the Pt loading impact the shape, activity and stability of Pt/ITO?
Structure of Pt/ITO as a function of Pt Loading
- ECSA decreased with increasing Pt content (size)
- Impact of particle size (and shape) on ORR Activity?
As expected, the total observed current decreased with Pt loading.

What we are really interested in is the Pt specific, $j_k$, and mass, $j_m$, activities.

$$j_k = \frac{i(0.9V)}{A_{Pt}} \quad j_m = j_k \times ECSA$$

Specific activity: Balance between increasing particle size (increasing $i_k$) and loss of preferential faceting (decreasing $i_k$)

All values comfortably exceed the DOE 2017 automotive targets for Pt specific and mass activity.
Influence of the Pt/ITO Loading on the Electrochemical Stability
Pt/ITO Catalysts Have:
(1) Pt growth mechanism on ITO that leads to preferential \{111\} faceting
(2) Very high ORR activity
(3) Excellent Electrochemical Stability for 1000’s of potential cycles
(4) A Practical Loading Limitation of ~ 40 wt%
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Questions?