Graphene-based Electrodes for Electrochemical Energy Conversion

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Graphene for electrochemical devices

Properties

• Electron conducting
• High surface area
• Catalytic

Applications

• Batteries
• Supercapacitors
• Fuel Cells
• Sensors
• …
What is a fuel cell?

Electrochemical “Energy Conversion” Device

Fuel:
- hydrogen, alcohols, hydrocarbons, etc.

Efficient and quiet
Fuel cell operation

\[ H_2 \rightarrow 2H^+ + 2e^- \quad \text{(HOR)} \]
\[ \frac{1}{2} O_2 + 2e^- \rightarrow O^{2-} \quad \text{(ORR)} \]

Overall: \[ H_2 + \frac{1}{2} O_2 \rightarrow H_2O + \text{electricity} \]
Driving force?

**Ans.** The chemical potential difference between the reactants (H₂ + O₂) and the product (H₂O)
Cell losses

\[ \text{H}_2 \quad \rightarrow \quad \text{O}_2 \quad \rightarrow \quad \text{ORR} \quad \rightarrow \quad \text{HOR} \quad \rightarrow \quad \text{OH}^2^- \quad \rightarrow \quad \text{O}_2 \quad \rightarrow \quad \text{H}_2 \]

- Ohmic Loss
- Activation Loss for HOR
- Activation Loss for ORR
- Ohmic Loss
**Solid Oxide Fuel Cell (SOFC)**

- **Advantages**
  - Fuel Flexibility
  - Simpler System
    - (No humidity control, etc.)

- **Disadvantages**
  - Material/Part selection
  - Durability
  - Limited applicability

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**High Operating Temperature**

\[ > 800 \, ^\circ C \]

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**Lower Operating Temperature!**

\[ (< 400 \, ^\circ C) \]
Both ohmic and activation loss \(\propto \exp(E_a/kT)\)
To counteract the significant ohmic loss

Thinning the electrolyte < 100 nm


To counteract the significant electrode loss

Need a totally new material system because...

- Conventional perovskite-based electrodes
  → Not active at low temperatures

- Pt-based electrode
  → Expensive
  → Fast degradation
Try doped graphene

New air electrode (cathode) materials for LT-SOFCs

Doped Graphene?
Why graphene as the cathode?

- **Graphene (and its derivatives)**
  - Extraordinary thermal and electrical conductivities
  - High specific surface area (theoretically 2630 m²/g for single-layer)
  - Strong mechanical strength and flexibility
  - Excellent catalytic activity (Doped Graphene)

Qu et al. *ACS Nano*, 4, 1321, 2010
N-doped Graphene as an ORR catalyst in Fuel Cell

- Catalytically superior to Pt
- Highly durable
- Resistant to CO and methanol poisoning

Qu et al. *ACS Nano*, 4, 1321, 2010
Solution & symmetric cell preparation procedure

GO (Graphene Oxide)

1. Flake graphite powder
2. Expansion of graphite sheets
3. Oxidization using KMnO₄
4. Filtration with PTFE filter

NrGO (Nitrogen Doped Reduced Graphene Oxide)

1. GO solution + dicyandiamide (DCDA) + D.I. water
2. Teflon-lined auto-clave
3. Hydrothermal rxn. @ 140, 180°C
4. Sonication in the suspension (90% water + 10% MeOH)
Graphene-based electrode deposition

- rGO
- NrGO140
- NrGO180

YSZ preparation → Tape Masking → Plasma cleaning → Dropping electrode solution

Drying and re-dropping → Removing the mask → A symmetric cell

(a) rGO  (b) NrGO180
Electrochemical Impedance Meas.

Diagram showing a setup with Air, YSZ, and Au mesh electrodes. The circuit includes resistors (\( R_L \) and \( R_H \)) and constant phase elements (CPEs). The graph plots -Im(Z) vs. Re(Z) with experimental and fitted data points. Frequency markers are provided: 0.7 MHz, 0.7 MHz, and 10 kHz.
Oxygen Reaction Performance

Y. Jee et al. submitted
Thermal Stability over Time

\[ \text{ASR}_{ct} / \text{ASR}_{ct\text{-initial}} \]

- **Pt**
- **NrGO**

Time [h]

\[ R_L / R_{L\text{-Init.}} \]

Y. Jee et al. *submitted*
Thermal stability of Pt: accelerated agglomeration

Agglomeration of Pt

- Ostwald ripening $\rightarrow$ Loss of active sites for ORR

At 500°C for 5 hrs
Thermal stability: morphological
Thermal stability: defects & stoichiometry

XPS

- Oxygen
- Nitrogen

Atomic ratio [%]

As-dep. 250°C 350°C

Raman

- rGO
- NrGO180

Intensity ratio (G/D)

Annealing temperature [°C]

Y. Jee et al. submitted
Thermal stability: d-spacing

 NrGO180 (As - 350°C) : ~3.4Å

Y. Jee et al. *submitted*
Transitional alternative – low loading Pt with high durability

Pt needs to have high surface area
(i.e. highly porous or nanoparticle structure)

→ Significant agglomeration during operation
→ Significant reduction in active area
→ Needs to maintain high surface area structure
Thermal agglomeration of Pt

@ 500 °C

@ 600 °C
Suppression of ripening by ultra-thin oxide
Suppression of ripening by ultra-thin oxide
Suppression of ripening by ultra-thin oxide
EIS analysis
Summary

- N-doped graphene as a SOFC cathod
  - showed a great oxygen reaction performance and durability at < 400 °C
  - Still much engineering opportunity (interface w/ current collector; cheaper doping process, enhanced reaction sites, etc.)

- Oxide nano-coating for metal ripening
  - Few nm oxide coating suppressed metal ripening
  - Also enhanced the catalytic activity
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