Graphene-based Air Electrodes for Solid Oxide Electrochemical Cells

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Prof. Min Hwan Lee
School of Engineering
UCMERCED
UNIVERSITY OF CALIFORNIA, MERCED

Graphene for electrochemical devices

Properties

- Electron conducting
- High surface area
- Catalytic

Applications

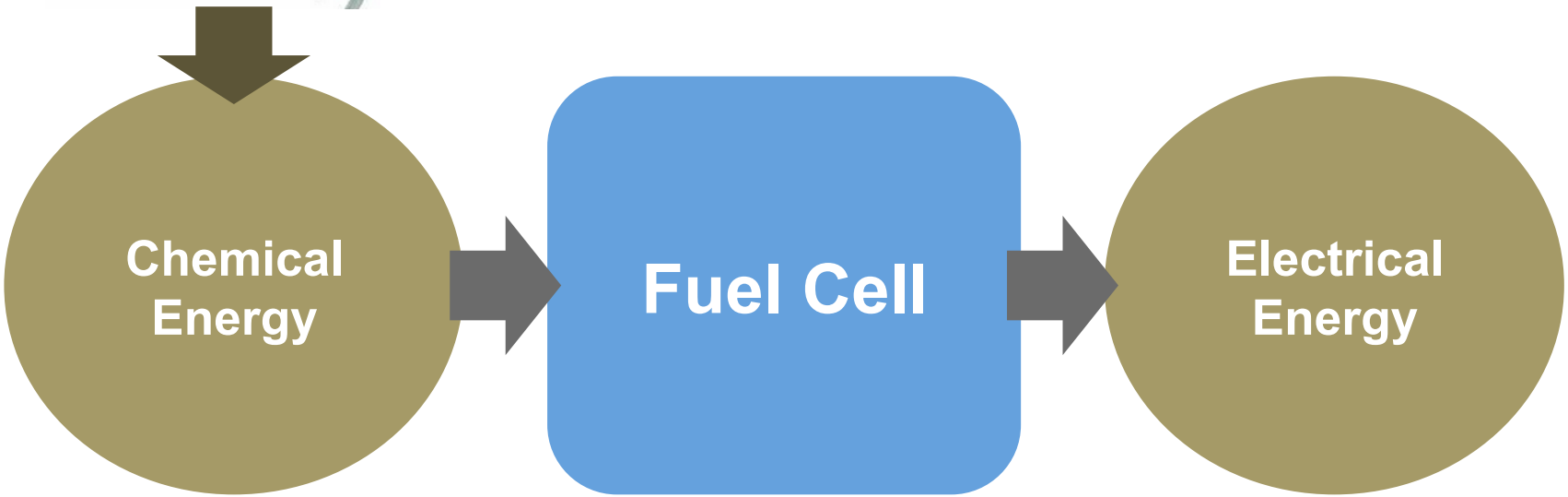
- Batteries
- Supercapacitors
- Fuel Cells
- Sensors
- …

What is a fuel cell?

Electrochemical “Energy Conversion” Device

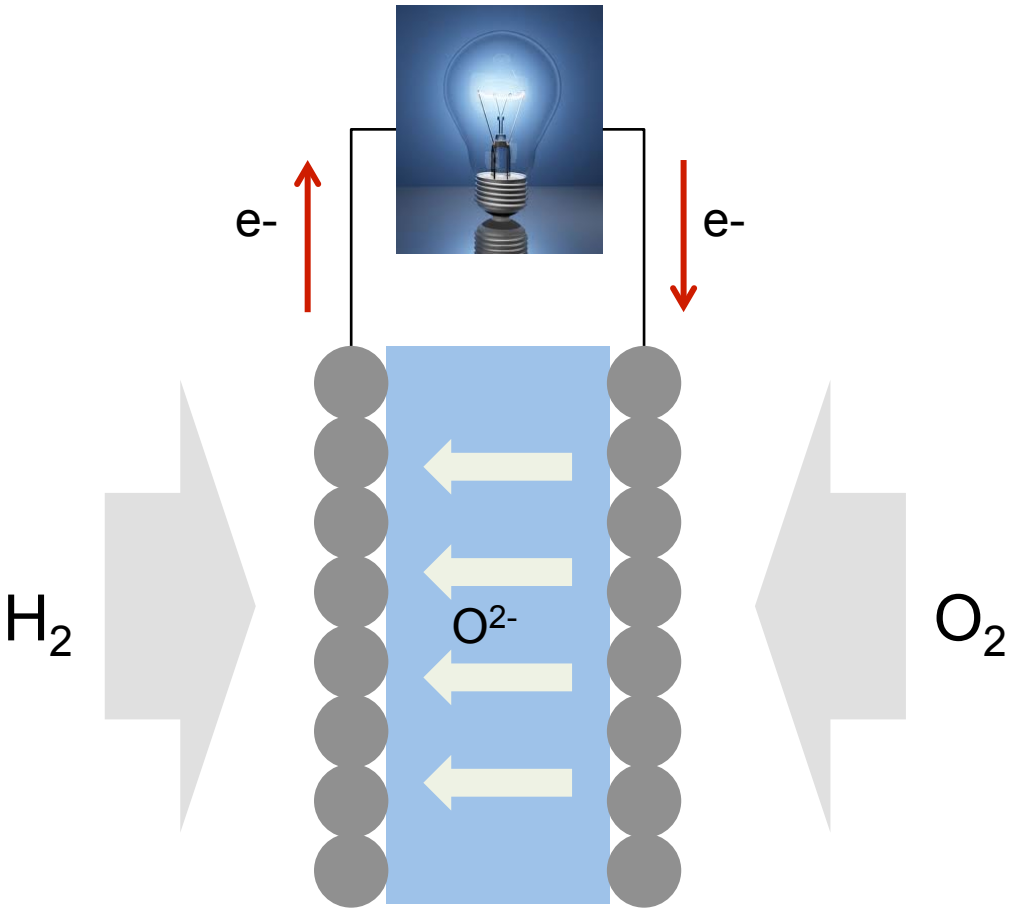
Fuel

: hydrogen, alcohols, hydrocarbons, etc.



Efficient and quiet

Fuel cell operation

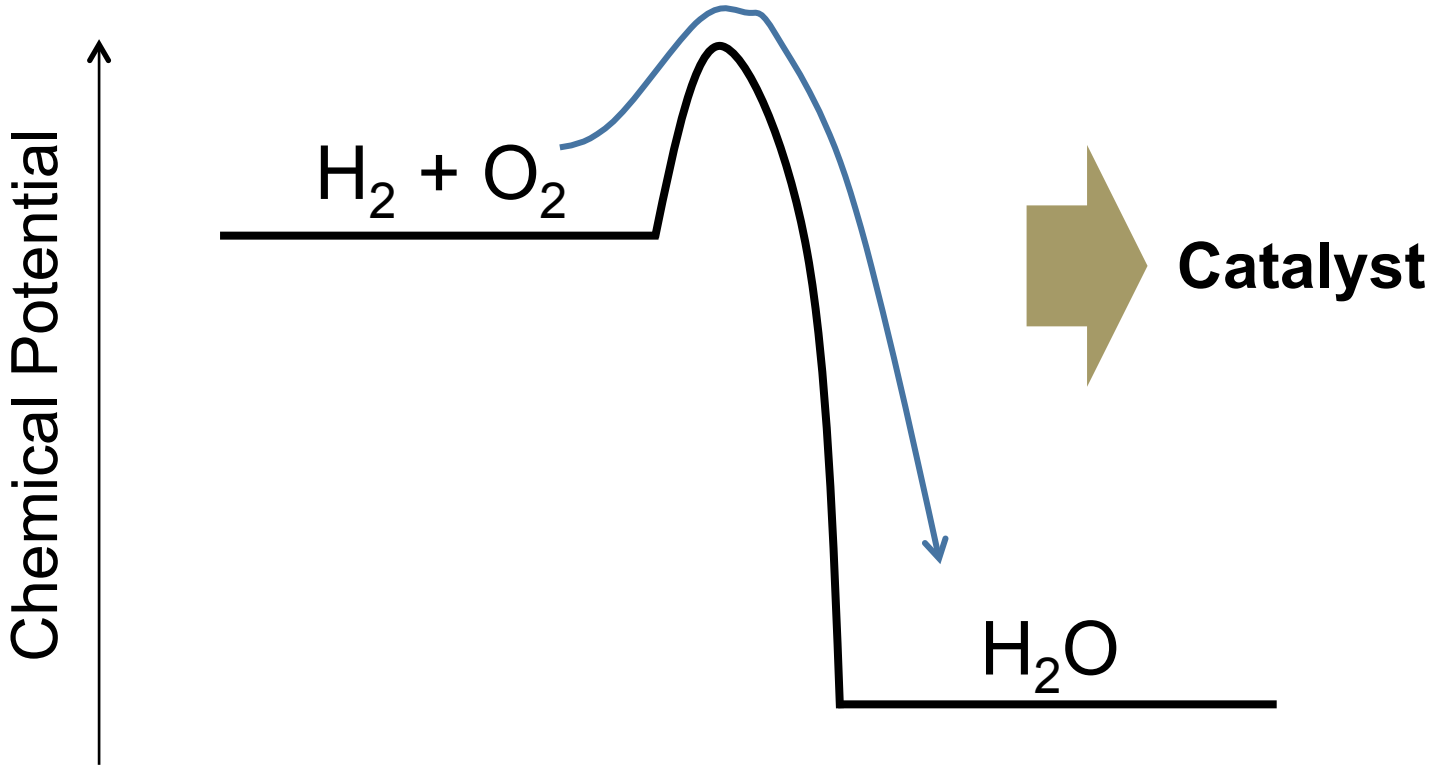


$H_2 \rightarrow 2H^+ + 2e^-$ (**HOR**) $\frac{1}{2} O_2 + 2e^- \rightarrow O^{2-}$ (**ORR**)

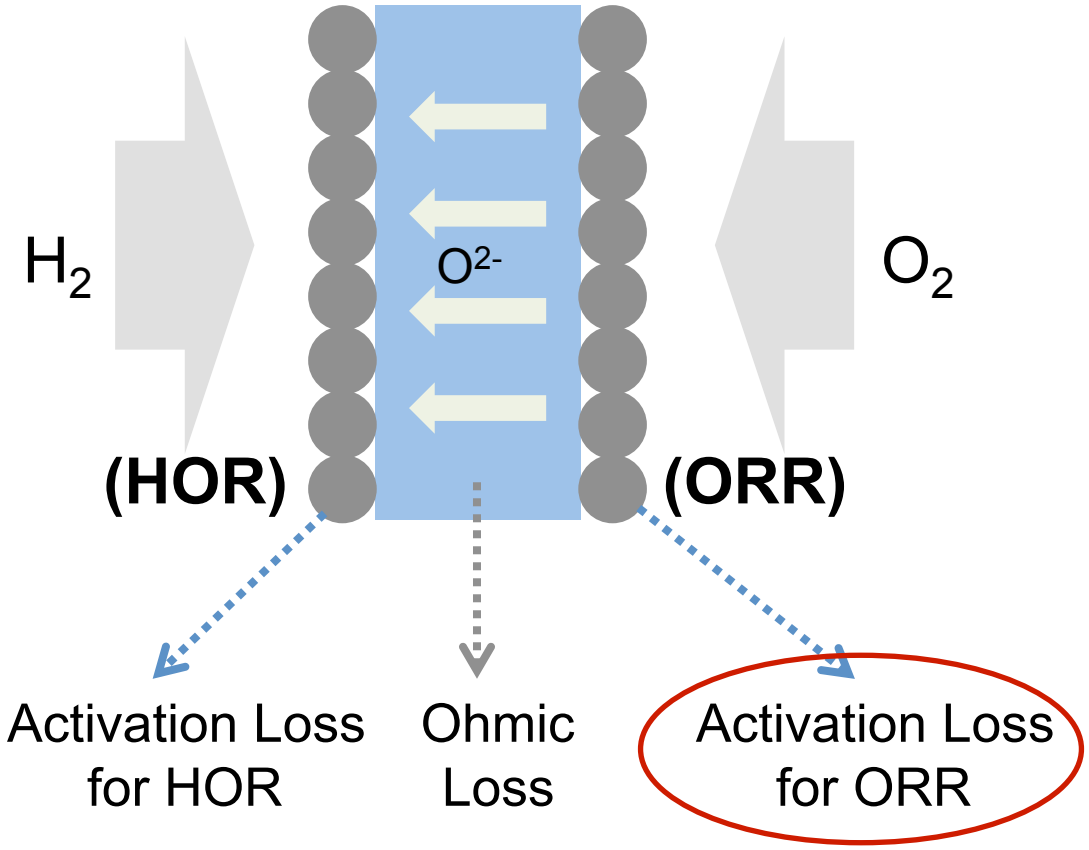
Overall: $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$ + electricity

Driving force?

Ans. The chemical potential difference between th e reactants (H_2 + O_2) and the product (H_2O)



Cell losses


H_2
O^{2-}
O_2
(HOR)
(ORR)
Activation Loss for HOR
Ohmic Loss
Activation Loss for ORR

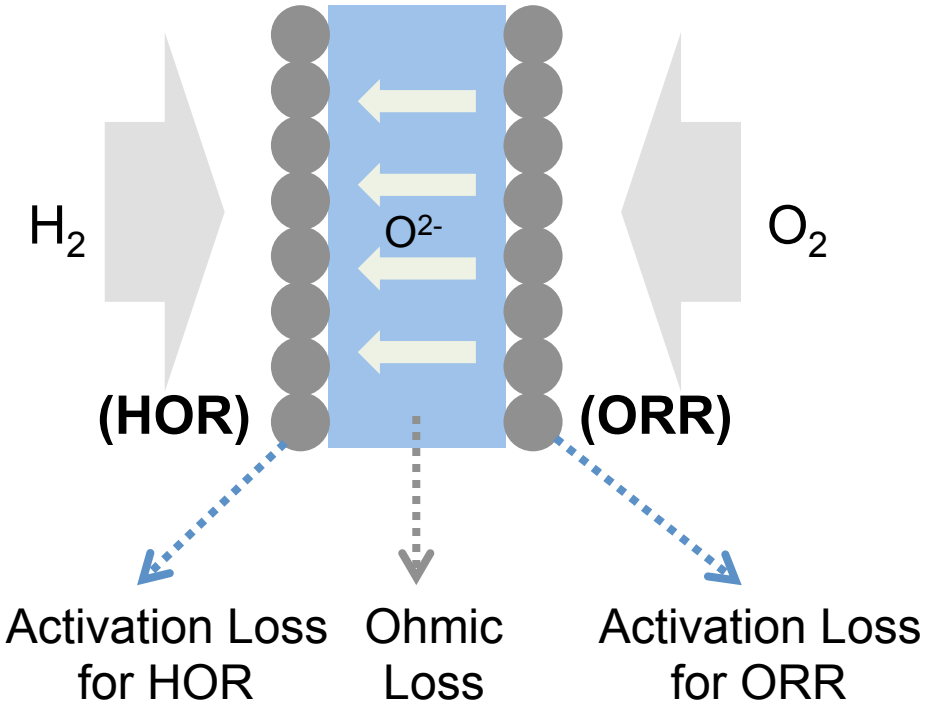
Solid Oxide Fuel Cell (SOFC)

High Operating Temperature
> 800 °C

- Advantages
  - →Fuel Flexibility
  - →Simpler System
    (No humidity control, etc.)
- Disadvantages
  - →Material/Part selection
  - →Durability
  - →Limited applicability

Lower Operating Temperature!
(< 400 °C)

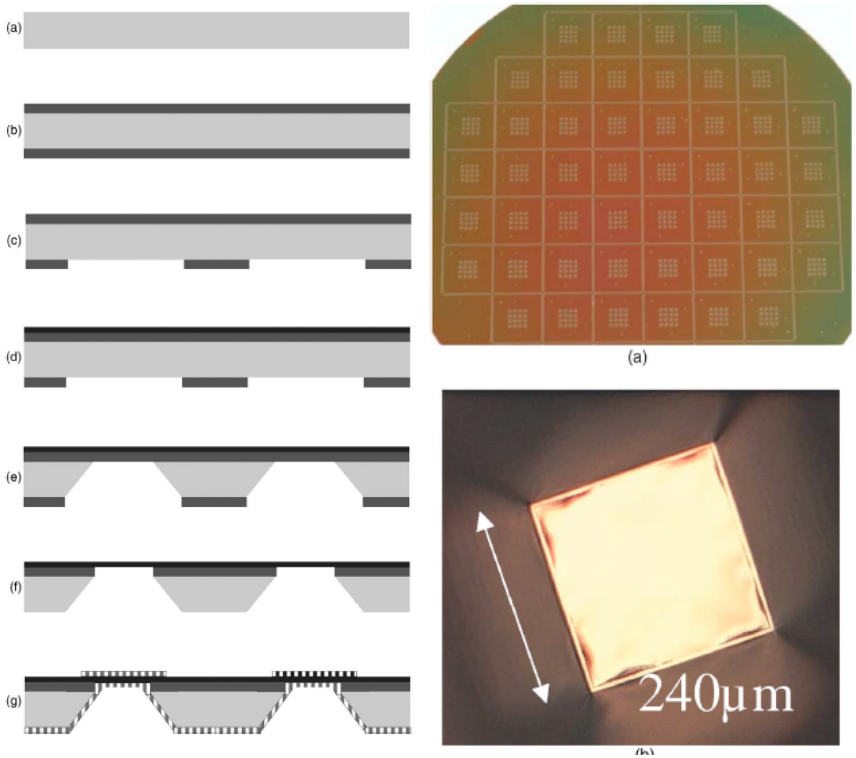
Reduction in T causes significant Losses!



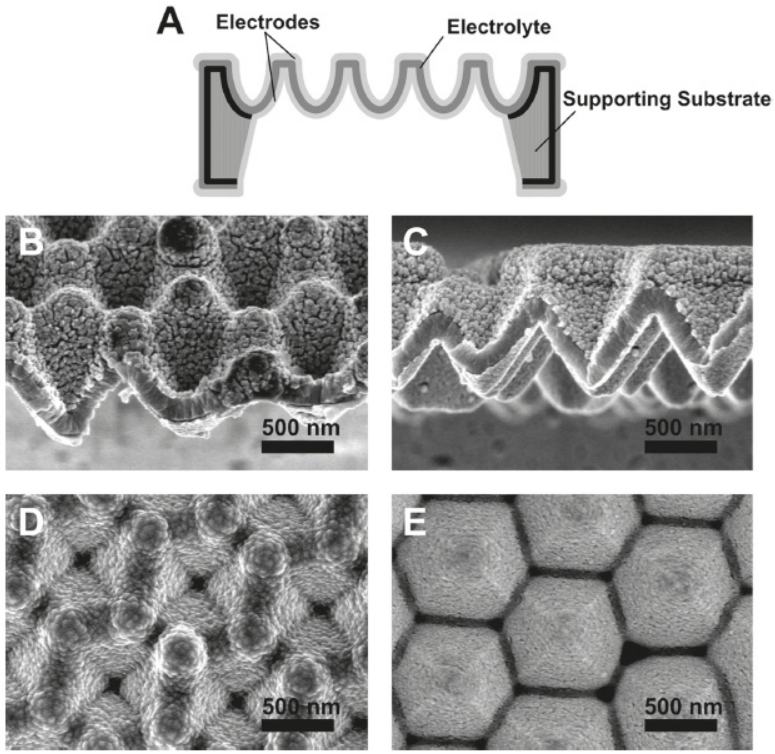
Both ohmic and activation loss $\propto$ $\boldsymbol{exp(E_a/kT)}$

To counteract the significant ohmic loss

Thinning the electrolyte < 100 nm



H. Huang et al. J. Electrochem. Soc., 154, B20, 2007



Y. B. Kim et al. Electrochem. Comm., 13, 403, 2011

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

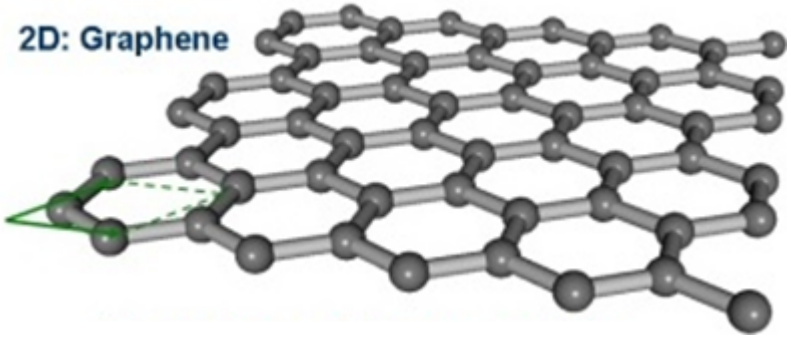
Objective

New air electrode (cathode) materials for LT-SOFCs

Doped Graphene?

Why graphene as the cathode?

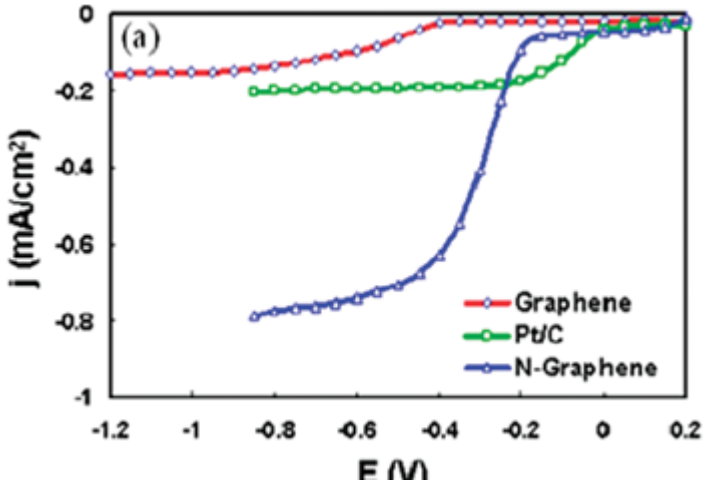
- **Graphene (and its derivatives)**
  - Extraordinary thermal and electrical conductivities
  - High specific surface area (theoretically 2630 m^2/g for single-layer)
  - Strong mechanical strength and flexibility
  - Excellent catalytic activity (Doped Graphene)



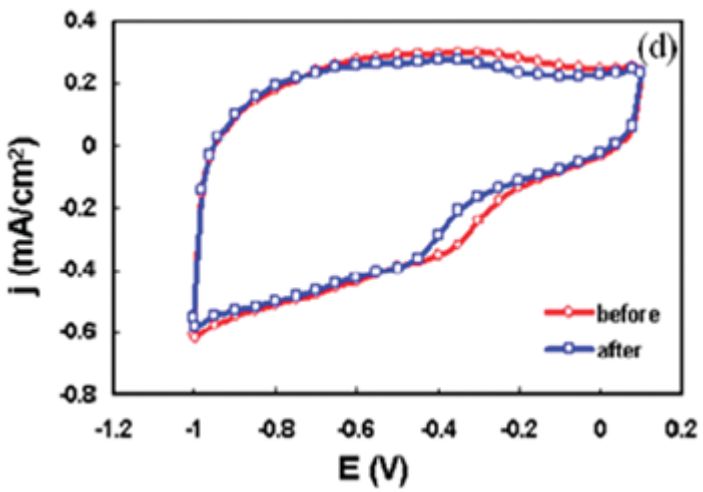
Qu et al. *ACS Nano*, 4, 1321, 2010

N-doped Graphene as an ORR catalyst in Fuel Cell

Catalytic Activity



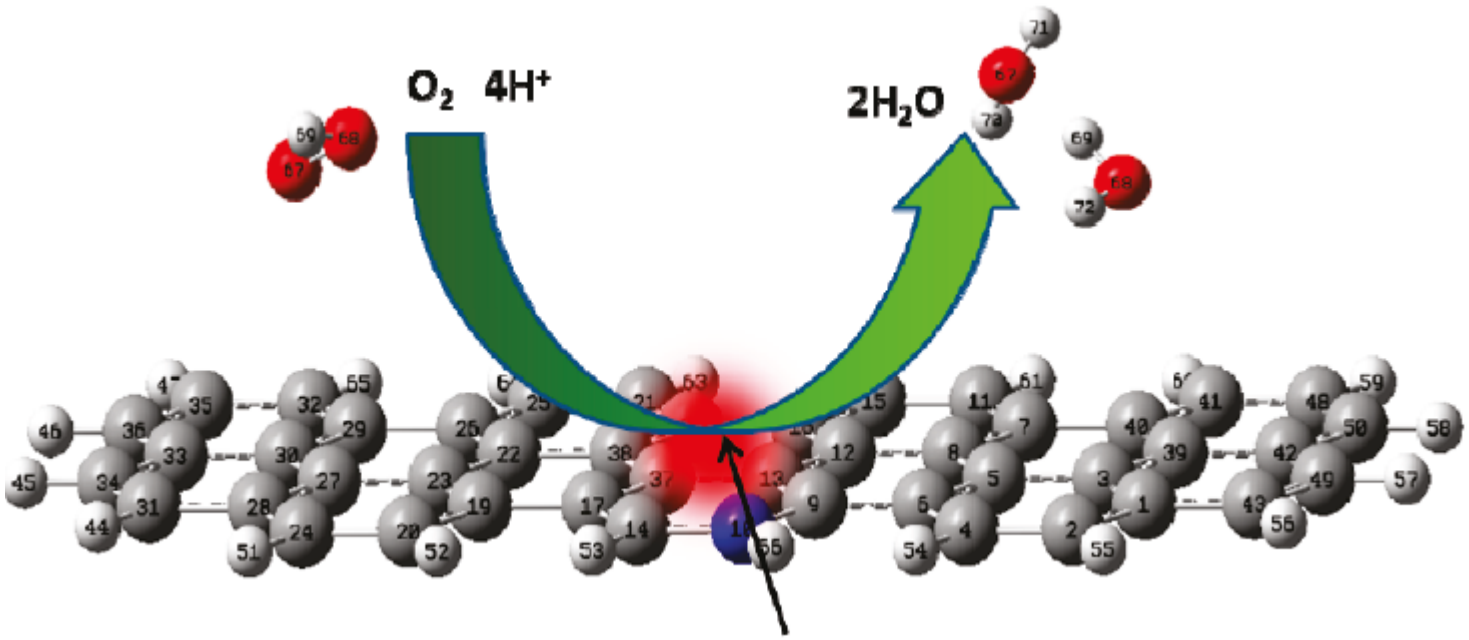
Durability over cycle (200k cy.)



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

Qu et al. *ACS Nano*, 4, 1321, 2010

How N-doping catalyze ORR ?



N-doping

Active site:
C with high spin density
or high charge density

L. Zhang and Z. Xia, *J Phys. Chem.*, 115, 11170, 2011

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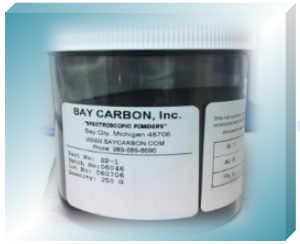
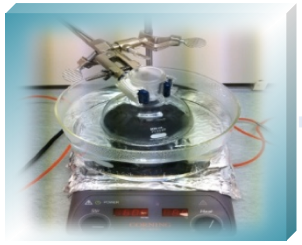
Solution & symmetric cell preparation procedure

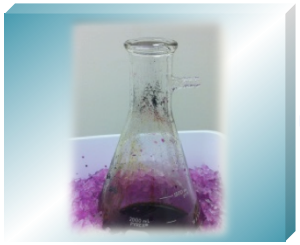
GO (Graphene Oxide)



Flake graphite powder

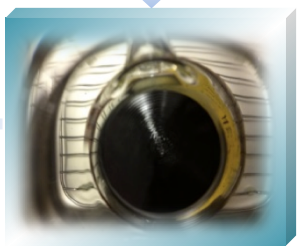


Expansion of graphite sheets



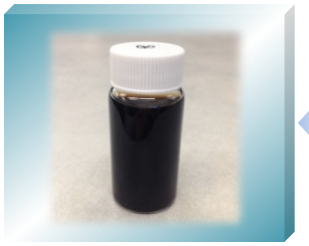
Oxidization using $KMnO_4$

Filtration with PTFE filter



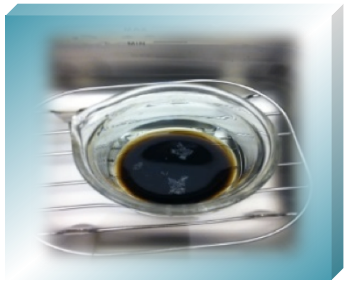
Sonication for better dispersion

Centrifuging to remove unexfoliated particles



Graphene oxide solution

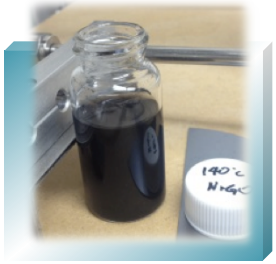
NrGO (Nitrogen Doped Reduced Graphene Oxide)



GO solution
+ dicyandiamide(DCDA)
+ D.I. water

Teflon-lined auto-clave

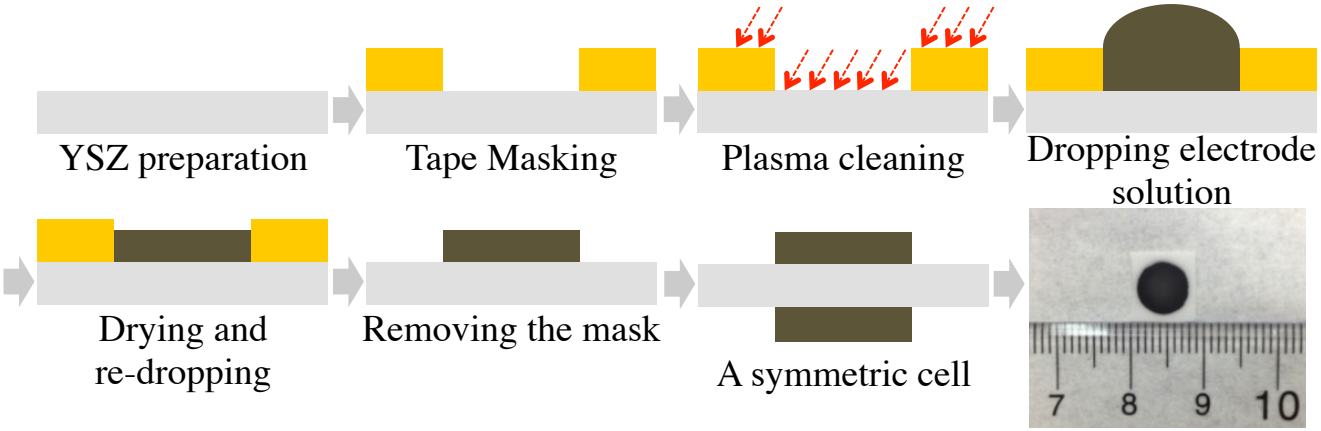
Hydrothermal rxn. @ 140, 180°C

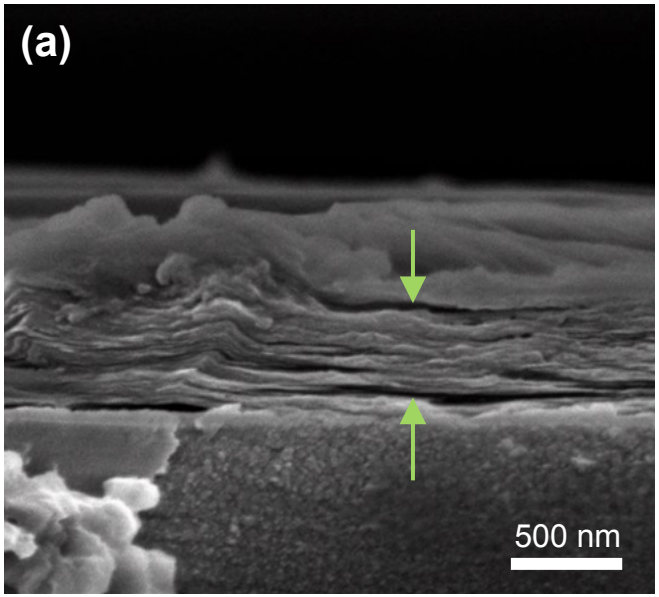


sonication in the suspension (90% water+10% MeOH)

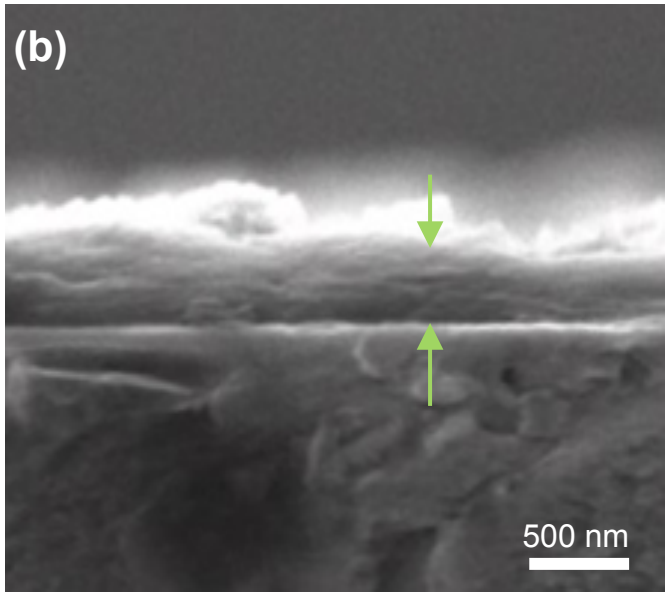
Graphene-based electrode deposition

- rGO
- NrGO140
- NrGO180



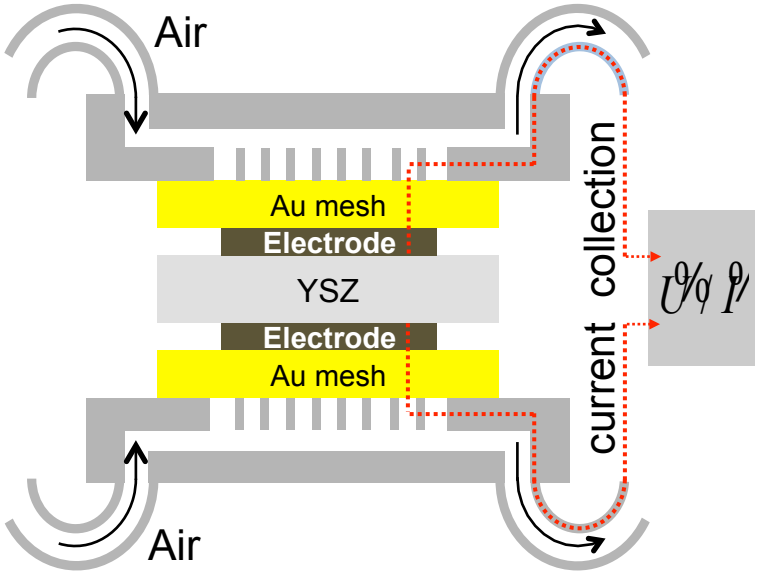


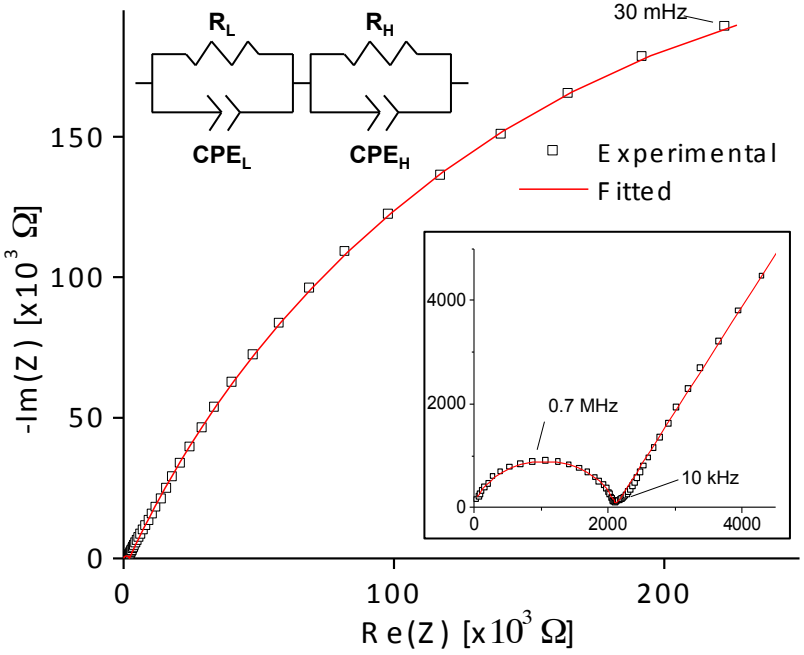
rGO



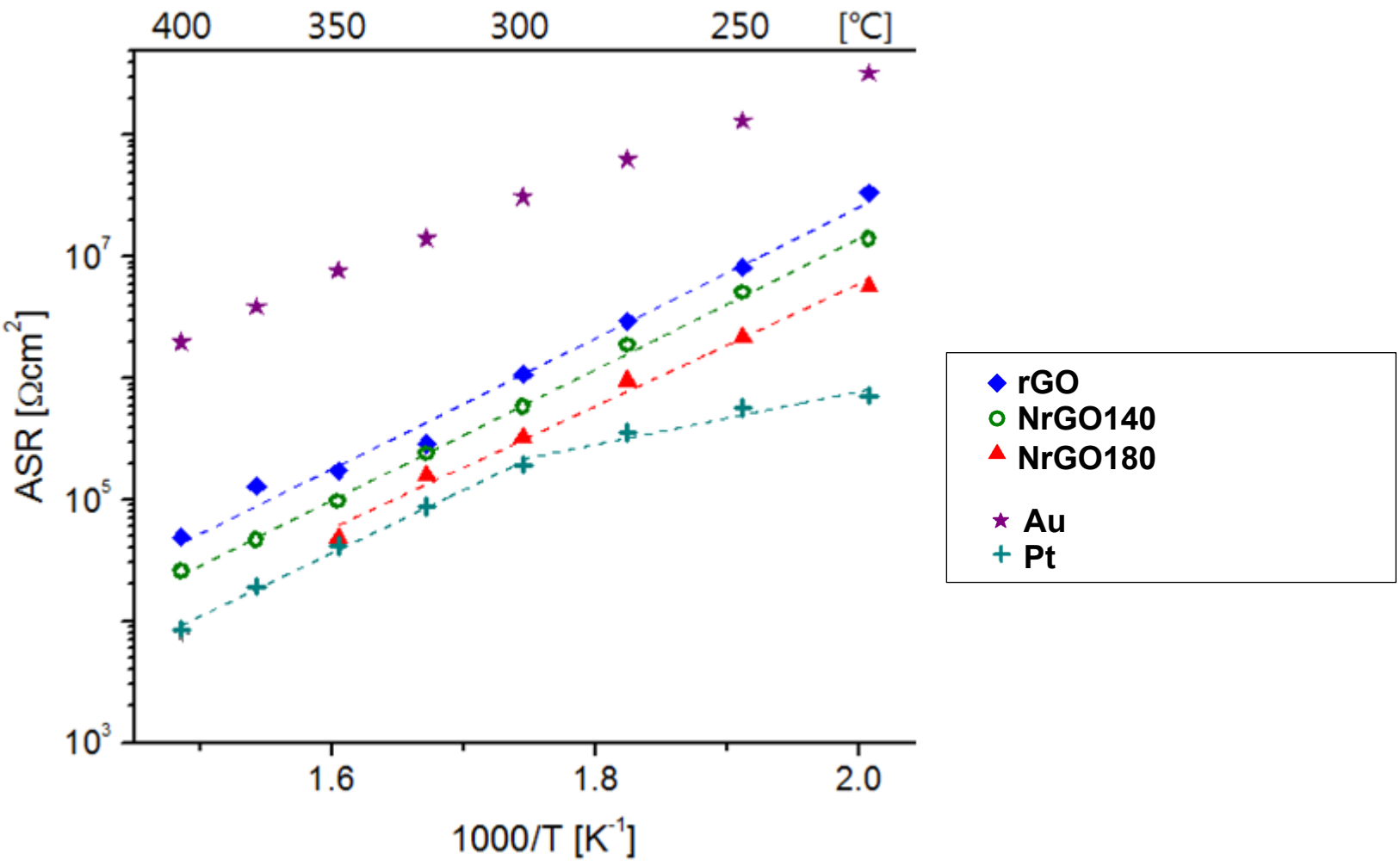
NrGO180

Electrochemical Impedance Meas.



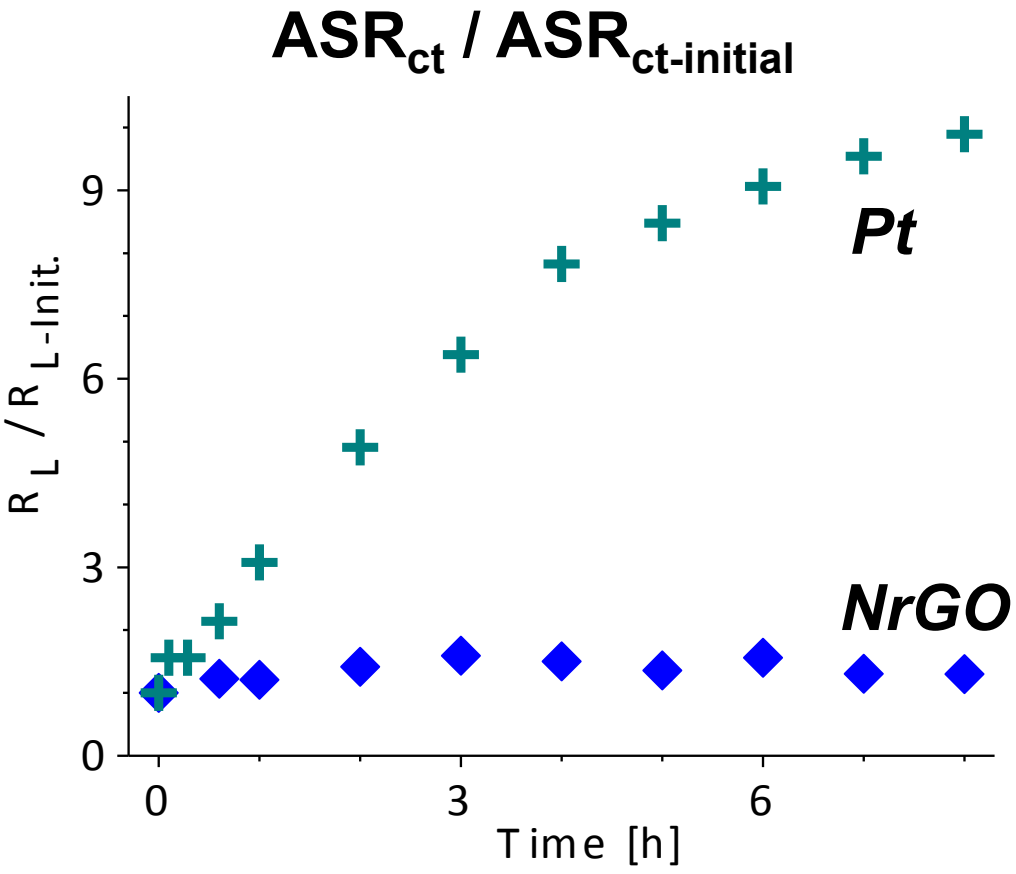


Oxygen Reaction Performance



Y. Jee et al. *submitted*

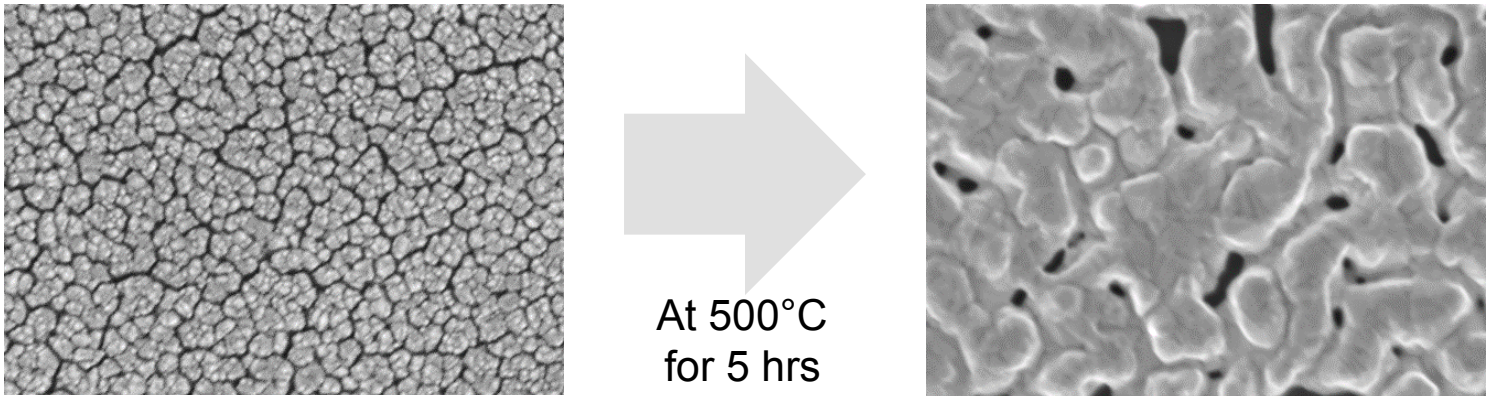
Thermal Stability over Time



Y. Jee et al. *submitted*

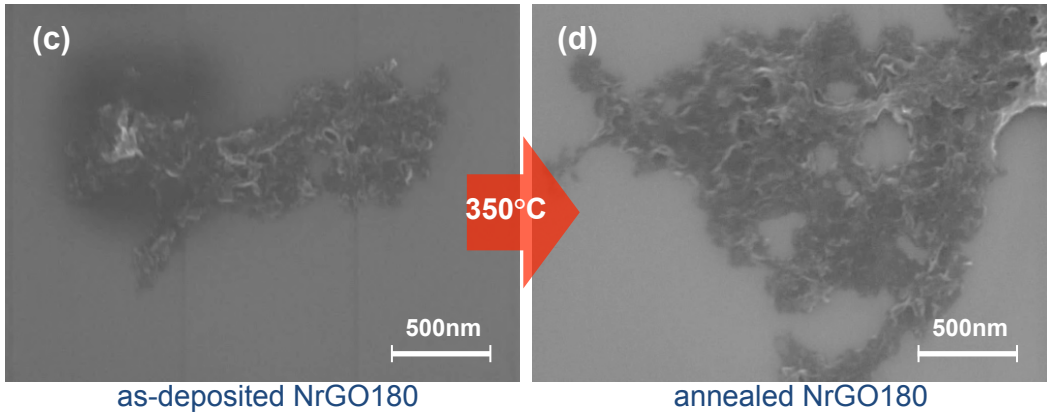
Thermal stability of Pt: accelerated agglomeration

Agglomeration of Pt

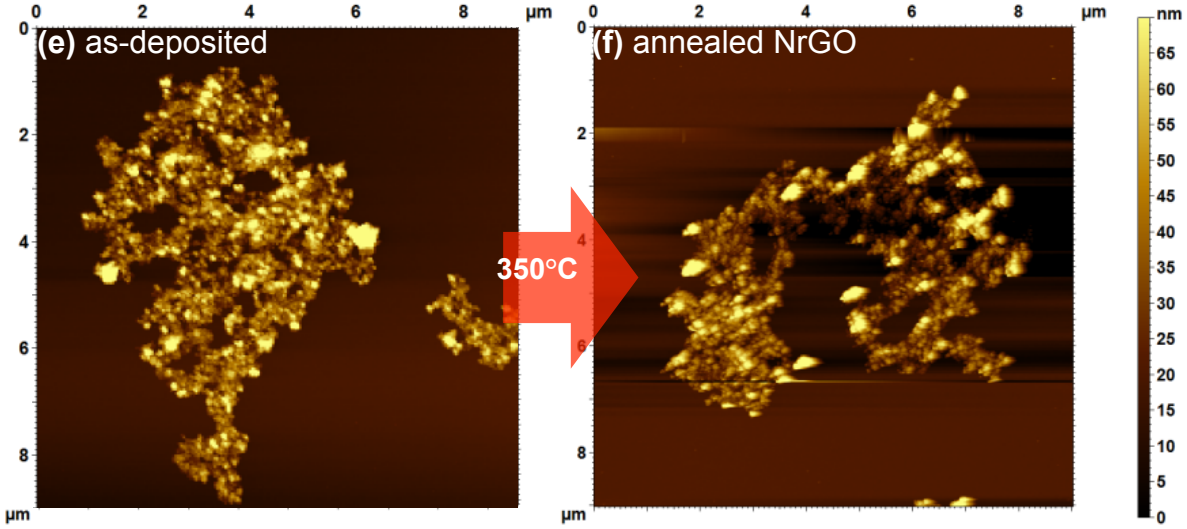


- *Ostwald ripening → Loss of active sites for ORR*

Thermal stability: morphological

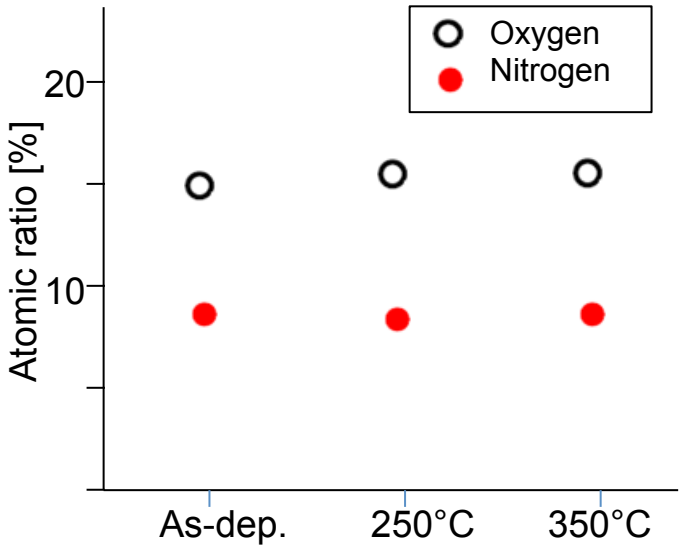


as-deposited NrGO180 annealed NrGO180

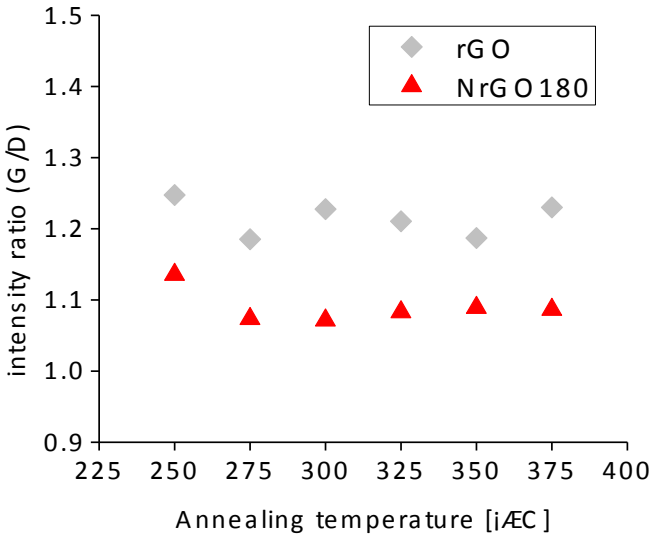


Thermal stability: defects & stoichiometry

XPS

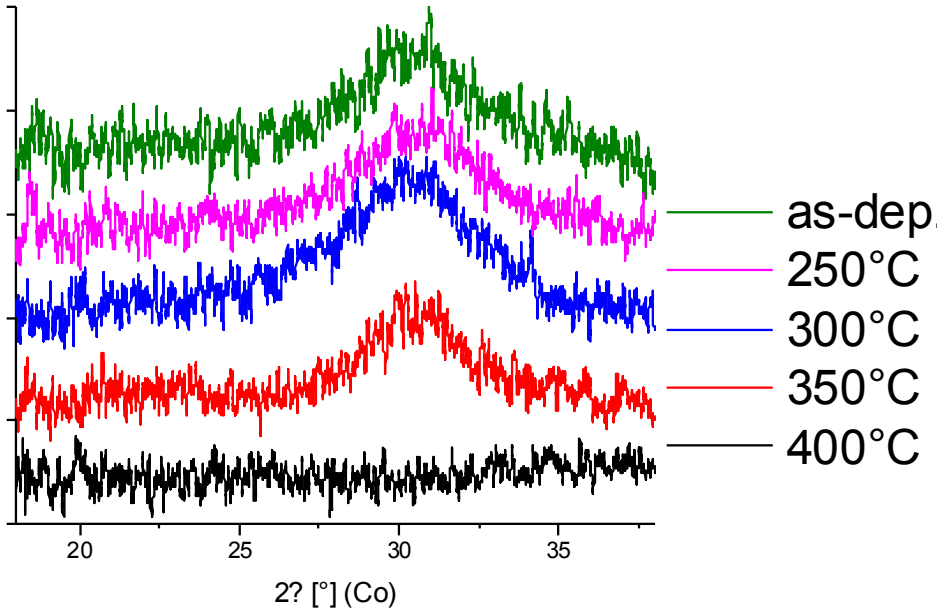


Raman



Y. Jee et al. *submitted*

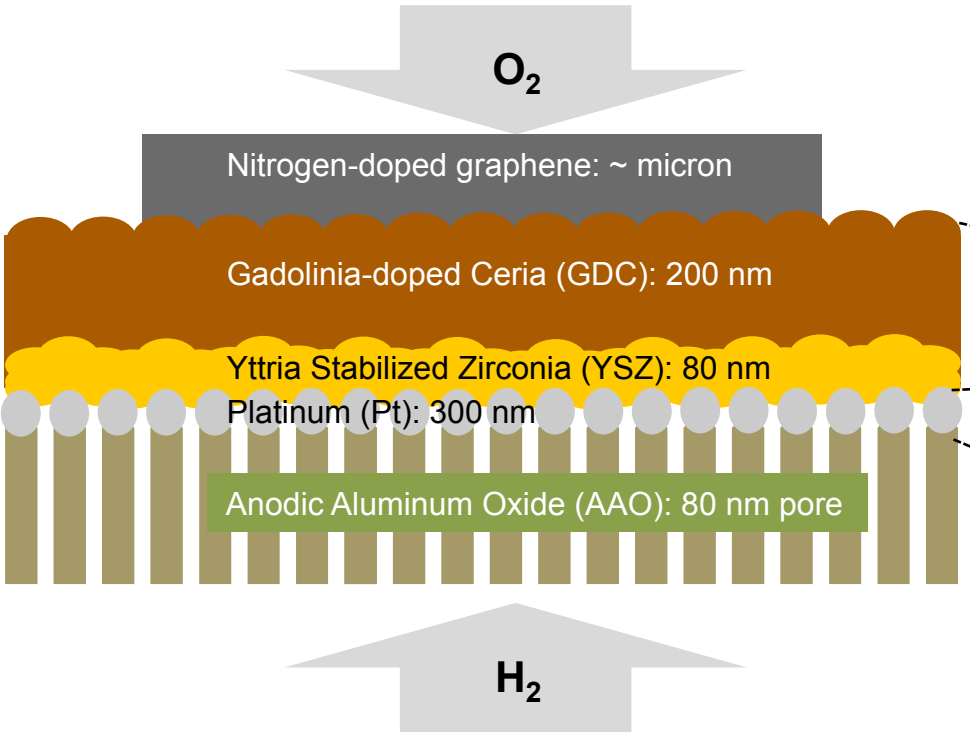
Thermal stability: d-spacing

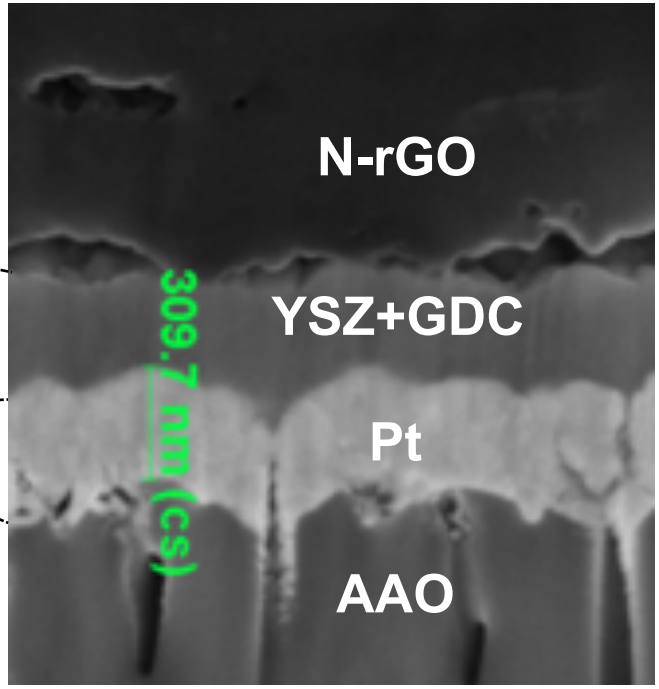


NrGO180 (As - 350°C) : ~3.4Å

Y. Jee et al. *submitted*

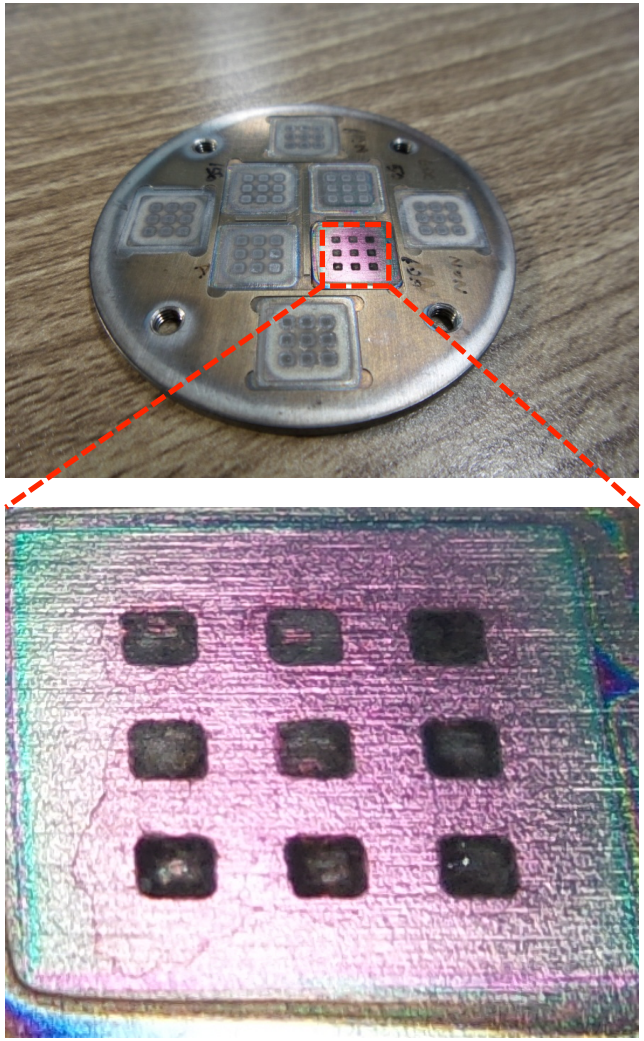
Cell Integration

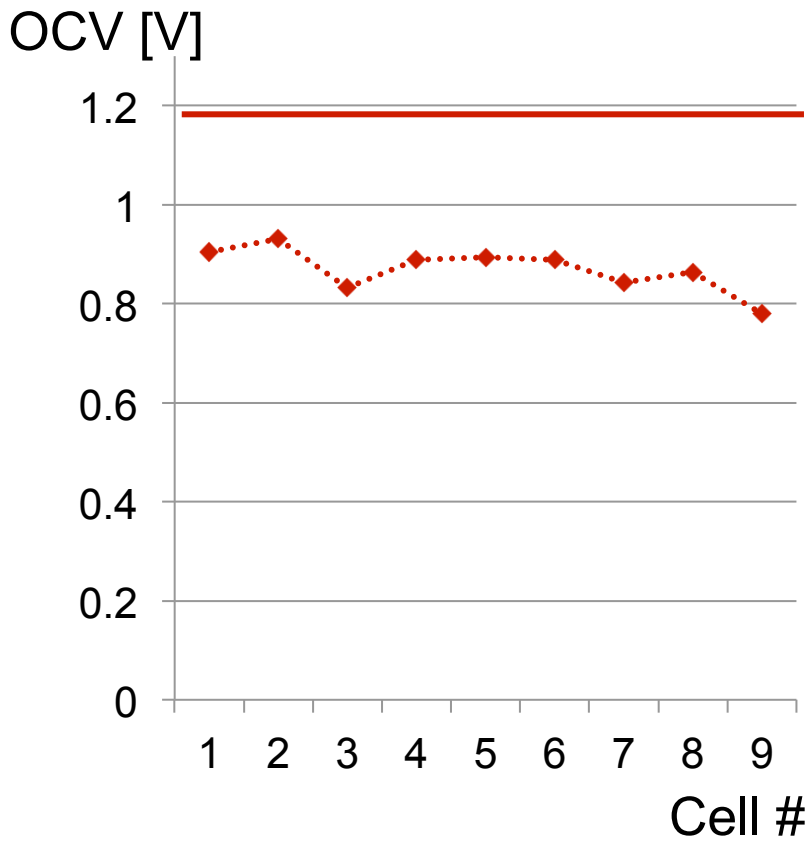




S. Ji et al. *In preparation*

Open Circuit Voltage





S. Ji et al. *In preparation*

Full Cell Performance

#	1	2	3	4	5	6	7	8	9
Peak Power Density (mW/cm^2)	0.1	0.25	-	0.08	0.08	0.02	0.04	0.13	0.09
Ohmic Resistance (Ωcm^2)	319	328	-	275	289	199	-	174	313

Most loss occurs at the electrolyte-NrGO interface

Summary

- LT-SOFC needs new air electrodes
  (Perovskites: poor catalysis; Pt: expensive and limited)
- N-doped graphene showed a great oxygen reaction performance and durability at < 400 °C
- Needs much engineering opportunity (interface w/ current collector; cheaper doping process, enhanced reaction sites, etc.)
- Good potential to be an alternative cathode material for LT-SOFCs

Acknowledgement

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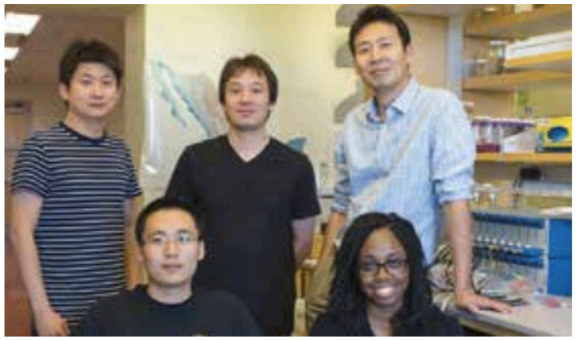
- Dr. Jihwan An and Prof. Fritz Prinz @ Stanford



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Thank you.

Min Hwan Lee
mlee49@ucmerced.edu