Electrochemical Energy Storage: Design Principles for Oxygen Electrocatalysts and Aqueous Supercapacitors

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Motivation: Powering the planet

Solar is the only renewable source capable of providing 20-50 TW of power worldwide.

Global power consumption: ~18 TW

Worldwide potential*: Wind < 4 TW, Biomass < 5 TW, Hydro < 1.5 TW, Geothermal < 1 TW, Solar ~ 120,000 TW

Cost of solar energy must be reduced.

We must store that energy.
Solar Materials and Electrochemistry Lab

Solar fuels

2H₂O → O₂ + 4H⁺ + 4e⁻
Fe
Ni
O

OER active site design?

interface theory

scalable III-V semiconductors for PV

GaAs(P)

Ga₂O(g) + As₂(g)

powder source

GaAs grown through mask

SiO₂ mask

1 μm

GaAs film

electrochemical capacitors

nano porous carbon

redox electrolyte

current collector

precise precursors

precise precursors

interface S P M

center for sustainable materials chemistry

Shannon Boettcher – Electrochemical Energy Storage
Solar fuels synthesis using semiconductors and electrocatalysts

Oxygen electrocatalysis has broad importance

- Solar water splitting
- Fuel-cells (ORR)
- Large scale electrolysis
- Air-breathing batteries

http://protononsite.com/
Need for well-defined systems and clean measurements

- Designed for maximum current per geometric area
- Dark colored – poorly suited for integrating in solar fuels systems

What is the role of composition, conductivity, and porosity?

What is the surface-active component?

Complicated!


From Wang et al., Electrochimica Acta, 2005, 50, 2059–2064
How do we design well-defined catalysts? What determines their activity?

James Ranney

Team Catalyst c. 2011

Kerisha Williams (Dr.) Lena Trotochaud
Solution-processed ultra-thin film catalysts

Advantages for fundamental study:

- Catalyst electrical conductivity (largely) irrelevant
- Film composition controlled exactly by precursor solution
- Mass known
- Surface area controlled
- Facile gas and ion transport

~50 wt% surfactant
~ 0.05 M metal nitrate ethanol

Initial target: Ni-Co-O

Mixing Co and Ni oxides reported = better performance.

Electronic? Chemical? Morphological?

\[ \text{H}_2\text{O} \rightarrow \text{*OH} \rightarrow \text{*O} + \text{H}_2\text{O} \rightarrow \text{*OOH} \rightarrow \text{O}_2 \]

* Indicates bonded to the surface

(see Rossmeisl, Norskov, etc.)

Oxygen evolution with Ni$_x$Co$_{1-x}$O$_y$ films

Performance increases with increasing Ni content.

No synergistic effect apparent.

Apparent activity of “plain NiO” very high.

Why?

- steady-state (> 15-30 min/step), 1 M KOH (99.999%)
- Hg|HgO 1 M KOH reference (0.929 V vs. RHE at pH 14 or 0.112 V vs. NHE)
- $R_s$ 2-3 Ω via AC impedance

NiCo$_2$O$_4$ 20 μm film,\(^1\) pH 14

Samples containing NiO evolve as a function of time

after 6 hrs at 10 mA cm\(^{-2}\)

as synthesized

activity increases with time

Current Density, \( J \) (mA cm\(^{-2}\))

Overpotential, \( \eta \) (V) - \( iR_s \)

0.3 V vs. Hg|HgO

0.0

0.1

0.2

0.3

NiO\(_x\)

Ni\(^{2+}\)

Ni\(^{3+/4+}\)

h\(^+\), OH\(^-\)

Ni(OH)\(_2\)

NiOOH / NiO\(_2\)

in-situ formation of a NiOOH?

1M 99.999% KOH, 20 mV s\(^{-1}\)

XPS analysis confirms transition to Ni(OH)$_2$/NiOOH

Co substitution suppresses transformation to oxyhydroxide

CV curves collected after 6 hr conditioning:

1M 99.999% KOH, 20 mV s\(^{-1}\)

<table>
<thead>
<tr>
<th>sample</th>
<th>e(^{-}) per metal</th>
<th>e(^{-}) per Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoO(_x)</td>
<td>0.04</td>
<td>n/a</td>
</tr>
<tr>
<td>Ni(<em>{0.25})Co(</em>{0.75})O(_x)</td>
<td>0.07</td>
<td>0.27</td>
</tr>
<tr>
<td>Ni(<em>{0.5})Co(</em>{0.5})O(_x)</td>
<td>0.31</td>
<td>0.63</td>
</tr>
<tr>
<td>Ni(<em>{0.75})Co(</em>{0.25})O(_x)</td>
<td>0.61</td>
<td>0.82</td>
</tr>
<tr>
<td>NiO(_x)</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Alloying with Co suppresses formation of Ni(OH)\(_2\) / NiOOH during conditioning.
In-situ phase transformation

Rock Salt (NiO)  
* catalysis limited to surface *

Spinel (e.g. Co$_3$O$_4$)  
* catalysis limited to surface *

Brucite/Hydrotalcite (e.g. M(OH)$_2$/MOOH)  
* catalysis throughout bulk – “3D” *
Ni(OH)$_2$ electrochemistry studied extensively for alkaline batteries

Dennis Corrigan:
- Ni(OH)$_2$ films cathodically electrodeposited
- Fe increases OER activity
  - Fe added intentionally
  - or Fe impurities in electrolyte

Fe is incorporated into electrochemically conditioned NiOOH films

Thin-film OER catalyst quantitative comparison using an EQCM

<table>
<thead>
<tr>
<th>sample</th>
<th>( \eta ) @ ( J = 1 ) mA cm(^{-2} ) (mV)</th>
<th>Tafel Slope (mV dec(^{-1}))</th>
<th>at ( \eta = 300 ) mV</th>
<th>TOF (sec(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO(_x)</td>
<td>512</td>
<td>49 ± 3</td>
<td>1.3</td>
<td>0.0003</td>
</tr>
<tr>
<td>FeO(_x)</td>
<td>409</td>
<td>51 ± 3</td>
<td>4.5</td>
<td>0.0009</td>
</tr>
<tr>
<td>CoO(_x)</td>
<td>395</td>
<td>49 ± 1</td>
<td>7.6</td>
<td>0.0016</td>
</tr>
<tr>
<td>IrO(_x)</td>
<td>381</td>
<td>42 ± 1</td>
<td>24.2</td>
<td>0.014</td>
</tr>
<tr>
<td>(Fe) Ni(<em>{0.5})Co(</em>{0.5})O(_x)</td>
<td>321</td>
<td>35 ± 2</td>
<td>273</td>
<td>0.056</td>
</tr>
<tr>
<td>NiO(_x) (Fe)</td>
<td>300</td>
<td>29 ± 0.4</td>
<td>773</td>
<td>0.17</td>
</tr>
<tr>
<td>Fe(<em>{0.1})Ni(</em>{0.9})O(_x)</td>
<td>297</td>
<td>30 ± 1</td>
<td>1009</td>
<td>0.21</td>
</tr>
</tbody>
</table>

TOF = \# O\(_2\) produced per metal per second

- Fe:NiOOH >10x more active than IrO\(_2\) and >100x more active than CoO\(_x\)
- Highest activity OER known in basic media. Why???

The role of Fe in NiOOH

- Crystal structure and (dis)order?
- “Energetics” of electronic states, i.e. “d-band” position?
- Film electronic conductivity?

![Diagram showing active site between sheets]

Active site between the sheets?

$E_{(Ni^{2+/3+})}$ shifts with [Fe]


Minimizing Fe Impurities

Activity increase with each cycle

Glassy C (GC) rotating disk electrode
Teflon cell, TraceSelect KOH (< 36 ppb Fe)
99.999% Ni(NO₃)₂·6H₂O

Overpotential, \( \eta (V) - iR_u \)

1500 rpm

No applied potential required for Fe incorporation

X-ray photoelectron spectroscopy

Need to use Mg X-ray source

\( \text{Ni}_{0.75}\text{Fe}_{0.25}(\text{OH})_2 \) (25% Fe)

5 CV cycles 5% Fe

No V applied 2% Fe

as deposited 0% Fe
Electrolyte Purification

- Precipitate Ni(OH)$_2$
  - TraceSelect KOH and 99.999% Ni(NO$_3$)$_2$·6H$_2$O
- Wash/centrifuge/decant
- Add electrolyte and shake…

No Fe after 300 CV cycles

Role of 3D structure?

Is $\beta$-NiOOH actually more active? Previous reports contain Fe?

“Crystallized” Ni(Fe)OOH

Peaks shift with crystallization of β-NiOH₂ - activity increases

No significant change in OER activity with crystallization

Trotochaud, Young, Ranney, Boettcher, S.W. J. Am. Chem. Soc. 2014.
Fe-Free NiOOH after crystallization

- New peak formation – minimal peak shift
- No increase in activity
- NiOOH very poor OER catalyst without Fe
• Aging increases long-range order
• Fe co-deposition gives larger inter-sheet spacing

Order and sheet spacing apparently not (strongly) related to activity.
Does Fe change electronic conductivity under OER conditions?

For 100 nm NiOOH film at 10 mA cm\(^{-2}\), <1 mV drop

\[ \sigma = \frac{I_{\text{cond}} w}{Nl d \Delta V} \]

Not important mechanism for activity enhancement
Other mixed metal oxyhydroxides?

Overpotential $\eta (V) - iR_u$

Current Density (mA cm$^{-2}$)

Potential (E(V) - $iR_u$ vs. Hg/HgO)

Effective Conductivity (S cm$^{-1}$)

OER onset near conductivity onset for FeOOH

Michaela Burke

Burke, Kast, Trotochaud, Boettcher, near submission to JACS 2014.
OER mechanism in (oxy)hydroxides

- NiOOH bad OER catalyst – low activity
- FeOOH has low conductivity thus low apparent activity
- Fe active site likely; modulated by NiOOH / CoOOH electrically conductive “porous” framework

* See also recent theory / XAS from Norskov, Bell

- Conductive NiOOH/CoOOOH = strongly coupled cations; delocalized electrons
A revised volcano plot

Previous Trend:
Ni > Co > Fe > Mn
“oxophilicity” of cation

Real Trend:
NiFe > CoFe > Fe > Co > Ni
Exact opposite


- Design better catalysts
- Integration with AEM
Semiconductor-catalyst interfaces


Part II: Redox-enhanced electrochemical double layer capacitors

David Ji
Xingfeng Wang

Sangeun Chun

Galen Stucky
Brian Evanko
Traditional electrochemical double-layer capacitors

Pros: power, cycle-ability
Cons: carbon cost, flammable electrolyte, low specific/volumetric energy

energy = \frac{1}{2}CV^2

• Merits (vs. EDLC)
  − electrolyte weight as active component
  − increased capacity / specific energy
  − use of aqueous electrolytes with high solubility (limited by low V)

• Challenges
  − self-discharge
  − maintain cycleability and high power

Redox electrolyte “design principles”

- use aqueous electrolyte (safety, cost)
- need different redox processes at negative and positive electrodes
- formal potentials near solvent window (energy)
- high solubility (energy)
- fast kinetics (power)
- stable (cyclability)
- design for slow self discharge??

**Potential redox couple species**

Need:
- high solubility
- large $\Delta V$ btw. couples
- fast kinetics
- slow self discharge

$\text{MV} = \text{methyl viologen}$
Three electrode cell design

- Activated carbon prepared by standard CO$_2$ activation process
- Electrode pellet - AC (85 %) : PTFE (10 %) : Acetylene black (5 wt.%)

10 mg per electrode, ~220 um thick
Control inert electrolyte

C = Q/V  energy = 1/2CV^2
Halogen electrolytes for positive electrode

Three electrode Swage-lock cell used to monitor both electrode processes simultaneously.

charging at 1 A/g
**Self-discharge dynamics**

- $I^-$ and $Br^-$ show *slow* self-discharge rate (specific absorption)
- $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ redox couple shows *fast* self-discharge
- $Co(bpy)_3^{2+}/Co(bpy)_3^{3+}$ *extremely fast* self-discharge (electrostatics)

\[
3Br^- \rightarrow Br_3^- + 2e^-
\]

Redox electrolytes for positive electrode

\[ \text{H}_3\text{C-N-}\text{NCH}_3^+ \]

\( \text{MV} = \text{methyl viologen} \)

- MV\(^+\) specific absorption slowing self-discharge?

\begin{align*}
\text{Cell potential, } E & (V_{\text{cell}}) \text{ or } E (V \text{ vs. SCE}) \\
\text{Potential, } E & (V) \\
\text{Time, } t & (\text{s}) \\
\text{Energy retention, } \eta & (\%) \\
\text{Open circuit period, } t & (\text{h})
\end{align*}
**Combined redox electrolytes**

1 M KBr/0.1 M MVCl₂

- Capacitive and faradaic responses evident on both electrodes
- Potentials separated by ~1.4 V – ideal in aq. electrolyte
**Combined redox electrolytes**

- Competitive over short times with non-aqueous cells
- Replace methyl with heptyl – decreases self discharge dramatically

\[
\text{HV}^{2+} \quad \text{N}^+ \begin{array}{c}
\text{N}^+ \\
\text{N}^+ \\
\text{N}^+ \\
\text{N}^+
\end{array} \quad \text{2Br}^-
\]
Power – energy – stability

Enhanced stability and solubility:

Nernstian electrochemical model

- symmetric electrodes, no separator
- agreement with experimental data
- improved performance possible

Brian Evanko
Summary: Redox Supercapacitors

- redox-active electrolyte = additional capacity
- electrostatics and specific absorption critical to prevent internal shunting
- record performance of ~15 Wh kg\(^{-1}\) for aq. redox capacitor
- >2000 cycles with heptyl-viologen
- useful niche between capacitor and battery?
Acknowledgements

Oxygen Catalysis

Michaela Burke

(Dr.) Lena Trotochaud

Interfaces

Dr. Fuding Lin

Theory and Simulation

T.J. Mills

Interfaces:
Basic Energy Sciences
Solar Photochemistry

OER Catalysis:

CSVT GaAs PV:

Redox Capacitors:

Thin Films:

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