Bifunctional Ceramic Fuel Cell Energy System
(Progress Report 2015-2016)

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About the Team

• University of South Carolina, Prof. Kevin Huang
  – energy storage materials, button cell testing, computational modeling
• University of Texas at Austin, Prof. John B. Goodenough
  – bifunctional oxygen-electrode materials
• University of Maryland, Prof. Eric Wachsman
  – oxygen isotope labeled surface exchange measurement
• Atrex Energy
  – pilot scale battery demonstration
Outline

- The concept
- Bi-functional oxygen-electrode development
- Button battery cell testing results
- Pilot-scale cell testing results
- Summary
About the Concept

Overall Reaction:

\[ Me + \frac{x}{2} O_2 \overset{\text{Discharge}}{\underset{\text{Charge}}{\rightleftharpoons}} MeO_x \]

\[ H_2(g) + O^{2-} \overset{\text{Discharge}}{\underset{\text{Charge}}{\rightleftharpoons}} H_2O(g) + 2e^- \]

\[ H_2(g) + MeO_x(s) \overset{\text{Charge}}{\underset{\text{Discharge}}{\rightleftharpoons}} H_2O(g) + Me \]

Solid Oxide Metal Air Redox Battery (SOMARB)

Energy & Environ. Sci., 2011, 4, 4942–4946
Modeling Predictions at 550°C

- Developing better oxygen electrode materials
- Improving Fe$_3$O$_4$-reduction (charging cycle) kinetics

*J. Power Sources, 280 (2015), 195-204*
The Donor (Ta, Nb, Y)-doped SrCoO$_{2.5+\delta}$

Ta-doped SrCoO$_{2.5+\delta}$ is a promising oxygen-electrode

*Journal of the Electrochemical Society, 163 (5) (2016) F330-F335*
Surface Oxygen Exchange Rate Measured by Oxygen Isotopic Exchange Method

- B-site doped SCO has a higher $k_{ex}$-value than A-site doped SCO
- For B-site doping, Nb>Fe
- For A-site doping, La>Y
- SCO based cathodes are 2 orders of magnitude higher $k_{ex}$ value than LSCF
σ-T-Po$_2$ Data of Nb-SrCoO$_{2.5+δ}$
$\sigma$-T-Po$_2$ Data of Nb-SrCoO$_{2.5+\delta}$

- $p$-type conductor
- Itinerant electron hole behavior
- Non-Arrhenius behavior
A New Defect Chemistry Model for Donor-doped SrCoO$_{2.5+\delta}$

- BM as a reference framework for point defect assignments
- Oxygen interstitials as ionic point defect
- Itinerant $d$-orbital electron holes as electronic point defect
Defect Reactions and Equilibria

Oxygen interstitial incorporation reaction:

\[
\frac{1}{2}O_2(g) + 2\text{Co}_\text{Co}^X + V_{I}^X \rightleftharpoons O_{I}'' + 2\text{Co}_\text{Co}^\cdot
\]

\[
K_{\text{ox}} = \frac{[O_{I}''][\text{Co}_\text{Co}^\cdot]^2}{p_{O_2}^{0.5}[\text{Co}_\text{Co}^X]^2[V_{I}^X]}
\]

Disproportionation reaction:

\[
2\text{Co}^X_{\text{Co}} \rightleftharpoons \text{Co}^\cdot_{\text{Co}} + \text{Co}'_{\text{Co}}
\]

\[
K_{\text{dsp}} = \frac{[\text{Co}^\cdot_{\text{Co}}] \cdot [\text{Co}'_{\text{Co}}]}{[\text{Co}^X_{\text{Co}}]^2}
\]

Charge neutrality:

\[
2[\text{Nb}^\cdot_{\text{Co}}] + [\text{Co}^\cdot_{\text{Co}}] = 2[O_{I}'''] + [\text{Co}'_{\text{Co}}]
\]

Co-site conservation:

\[
[\text{Co}^X_{\text{Co}}] + [\text{Co}^\cdot_{\text{Co}}] + [\text{Co}'_{\text{Co}}] + [\text{Nb}^\cdot_{\text{Co}}] = 1
\]

Oxygen-site conservation:

\[
[V_{I}^X] + [O_{I}'''] = 0.5
\]

Electron-hole conductivity:

\[
\sigma = [\text{Co}^\cdot_{\text{Co}}]c_0F\mu; \quad \mu = \frac{e\tau}{m^*}
\]
Experimental vs Modeled
Equilibrium Constants of Defect Reactions

\[ \frac{1}{2} \text{O}_2(g) + 2\text{Co}^\text{x}_\text{Co} + \text{V}_1^\text{x} \rightleftharpoons \text{O}_2'' + 2\text{Co}^\text{ox}_\text{Co} \]

\[ 2\text{Co}^\text{x}_\text{Co} \rightleftharpoons \text{Co}^\text{ox}_\text{Co} + \text{Co}^\text{ox'}_\text{Co} \]

\[
-\frac{\Delta H_{ox}^0}{RT} + \frac{\Delta S_{ox}^0}{R} = \ln K_{ox}
\]

\[
-\frac{\Delta H_{dsp}^0}{RT} + \frac{\Delta S_{dsp}^0}{R} = \ln K_{dsp}
\]
Concentration Contours of Nb-SrCoO$_{2.5+\delta}$
Thermodynamic Properties of Nb-SrCoO$_{2.5+\delta}$

\[
\frac{R}{2} \ln p_{O_2} = \frac{\Delta \bar{h}_O}{T} - \Delta \bar{s}_O
\]
Partial Molar vs Integral Molar Properties

\[
\Delta \bar{h}_0 = \frac{\partial [Co'_Co]}{\partial \delta} \Delta H_{dsp} + \Delta H_{ox}^0
\]

\[
\Delta \bar{s}_0 = \frac{\partial [Co'_Co]}{\partial \delta} \Delta S_{dsp}^0 + \Delta S_{ox}^0 + s_0 (conf)
\]
DFT Calculations Supporting the Formation of Oxygen Interstitials

(a) [Diagram showing crystal structure with labels for Sr, Co, O, Oy, and Nb sites]

(b) [Graph showing energy difference vs. reaction path with a peak at 1.136 eV for Pure SrCoO$_{2.5}$]

(c) [Diagram showing an additional Nb dopant]

(d) [Graph showing energy difference vs. reaction path with a peak at 0.505 eV for Nb doped SrCoO$_{2.5}$]
Evaluations of Button Cell Performance

- **Fe loading**: 0.056 g
- **Discharge/charge current**:
  - C/5.5: 12.7 mA (10 mA cm\(^{-2}\))
  - C/5: 14 mA (11 mA cm\(^{-2}\))
  - C/3: 23.4 mA (18.5 mA cm\(^{-2}\))
  - 1C: 70.1 mA (55.3 mA cm\(^{-2}\))
- **Depth of discharge (DoD) at 20%**
  - 1 h @ C/5
  - 36 min @ C/3
  - 12 min @ 1C
The Effect of Fe-Bed Catalysts on Battery Performance

500 °C; 10 mA cm² (C/5.5); 10 min discharge/charge; DoD=3%
Evaluations at Higher DoD (Fe-Utilization)

- 5wt% Pd-impregnated Fe$_2$O$_3$-ZrO$_2$
- Tested at 500°C
- Rate: 0.2C (11 mA/cm$^2$ or 250 mA/g)
- DoD=20%
- Charge/discharge duration: 1 hour
- Fe-loading: 0.056 grams
The Evaluation at Different C-rates
Comparison with Li-O₂ Battery

A Fe-Bed Installed Commercial Scale SOFC

Cathode reaction: \( O_2 + 4e' = 2O^{2-} \)

Anode reaction: \( 2H_2 + 2O^{2-} \rightarrow 2H_2O + 4e' \)

Fe-bed: \( H_2 + FeO \leftarrow Fe + H_2O \)
Installation of Fe-bed into Pilot-scale Cell at Atrex Energy
Overload Tolerance Capability (Current cycling with constant H₂ flow)
Fast Ramping Power Capability

- Power ramping rate: ±2.5 kW/min/cell
- Scaling from single cell to 1 MW system translates to 67 MW/min power ramping capability
Theoretical FEA Analysis
Potential Applications of Fe-bed SOFC Technology

• Fast loading following
  – to compensate for variable power sources, e.g. wind and solar, as their output fluctuates

• Frequency regulation
  – to synchronize electricity generation and load

• Demand charge management
  – to reduce the peak demand
Summary

• Donor-doped SrCoO$_{2.5+\delta}$ is a good IT bifunctional oxygen electrode
• A new defect chemistry model has been established
• Pd is an excellent catalyst for Fe$_3$O$_4$ reduction in H$_2$
• Performance of solid oxide Fe-air battery is evaluated at different DoD and C-rates
• Internal Fe-bed enables SOFCs to be overload-tolerant and load-responsive much needed for grid stability management
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