Bifunctional Ceramic Fuel Cell Energy System

(*Progress Report 2015-2016)*

Prof. Kevin Huang

University of South Carolina, Columbia, SC29201

Present to DOE NETL 17th Solid Oxide Fuel Cell project review meeting, July 19-21, 2016, Pittsburgh

About the Team

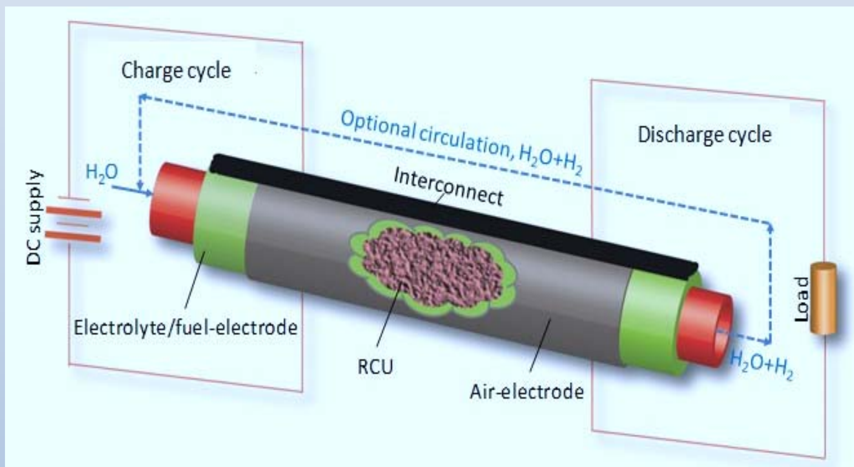
- University of South Carolina, Prof. Kevin Huang
  - energy storage materials, button cell testing, computational modeling
- University of Texas at Austin, Prof. John B. Goodenough
  - bifunctional oxygen-electrode materials
- University of Maryland, Prof. Eric Wachsman
  - oxygen isotope labeled surface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

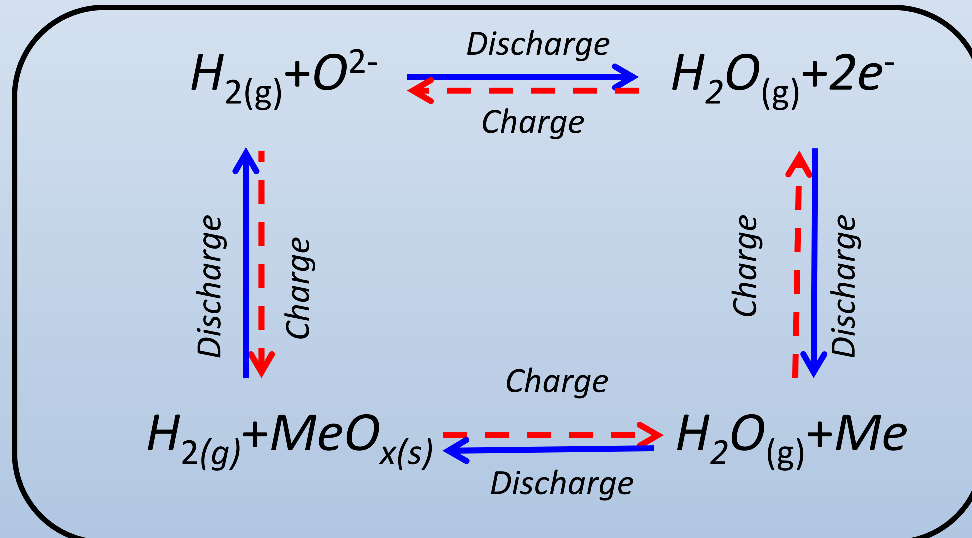
Outline

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

About the Concept

Overall Reaction: $Me + \frac{x}{2} O_2 \underset{Charge}{\overset{Discharge}{\rightleftarrows}} MeO_x$

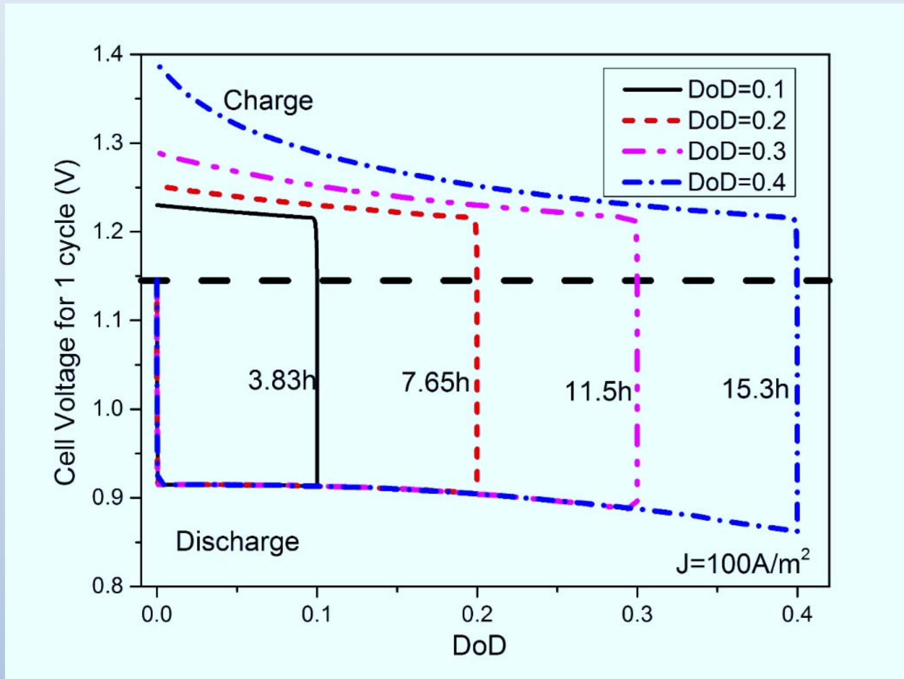


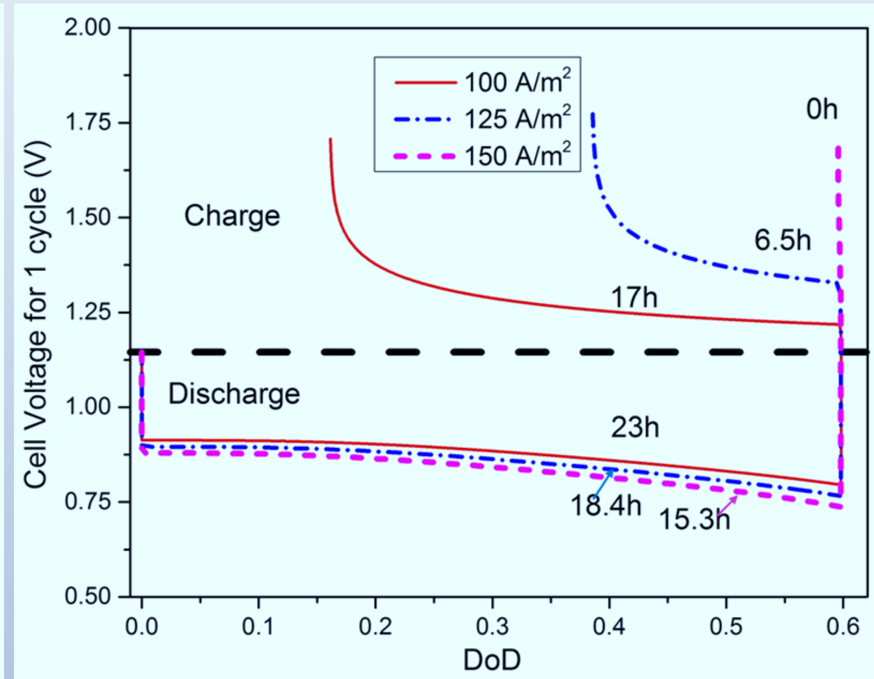


<u>S</u>olid <u>O</u>xide <u>M</u>etal <u>A</u>ir <u>R</u>edox <u>B</u>attery (SOMARB)

__Energy & Environ. Sci.__, 2011, 4, 4942–4946

Modeling Predictions at 550^{o}C

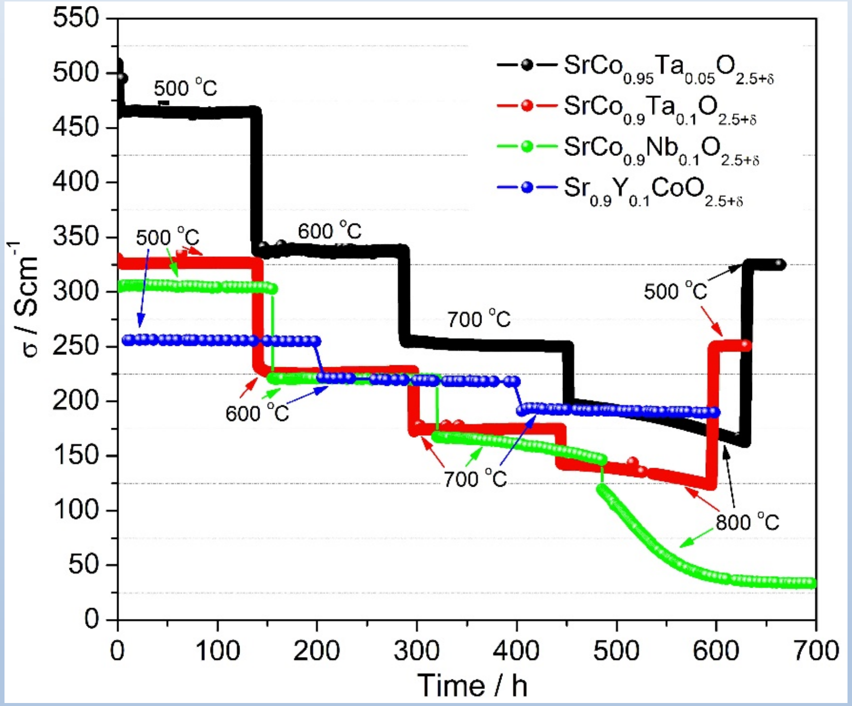


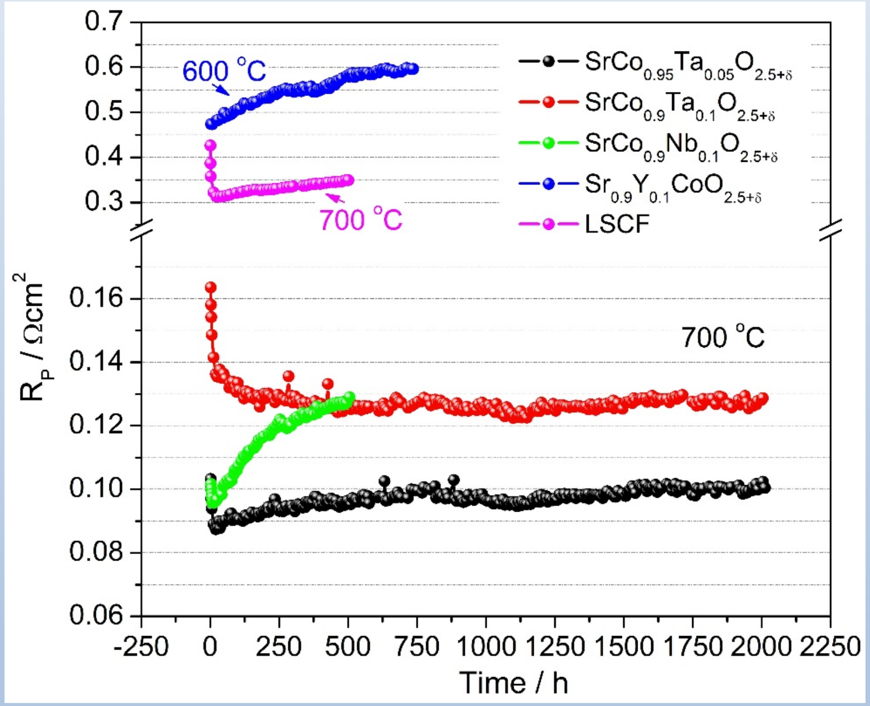


- Developing better oxygen electrode materials
- Improving Fe_3O_4-reduction (charging cycle) kinetics

J. Power Sources, 280 (2015), 195-204

The Donor (Ta, Nb, Y)-doped $SrCoO_{2.5+\delta}$

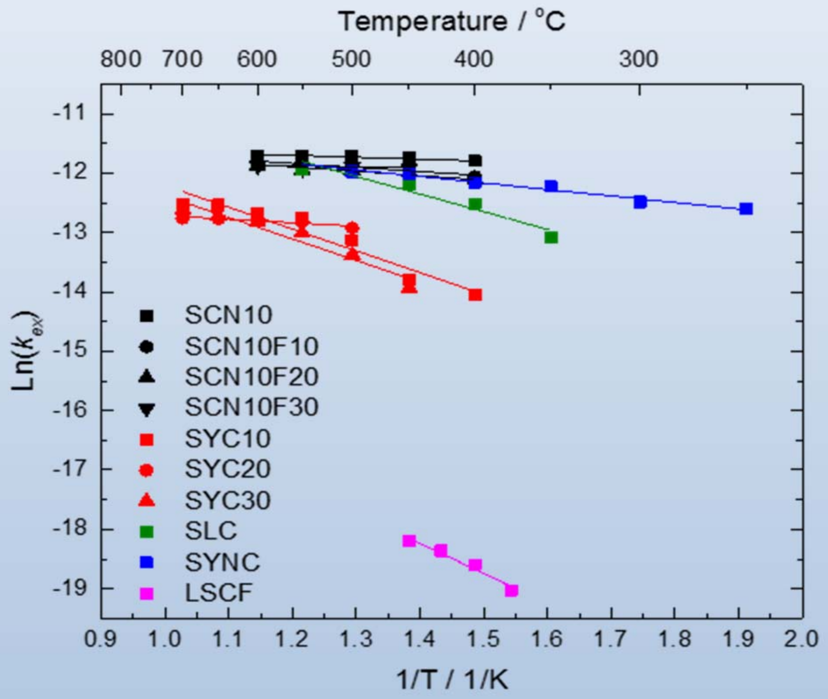


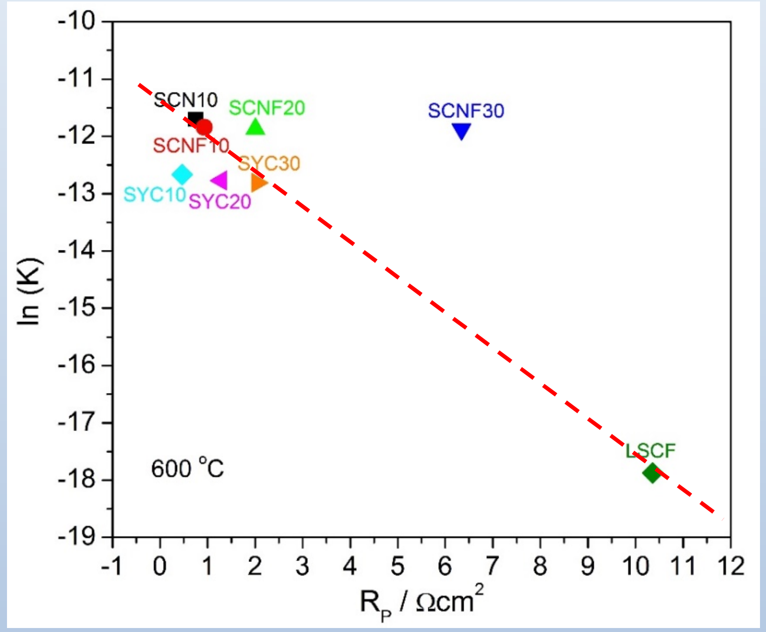


Ta-doped $SrCoO_{2.5+\delta}$ is a promising oxygen-electrode

__Journal of the Electrochemical Society__, 163 (5) (2016) F330-F335

Surface Oxygen Exchange Rate Measured by Oxygen Isotopic Exchange Method

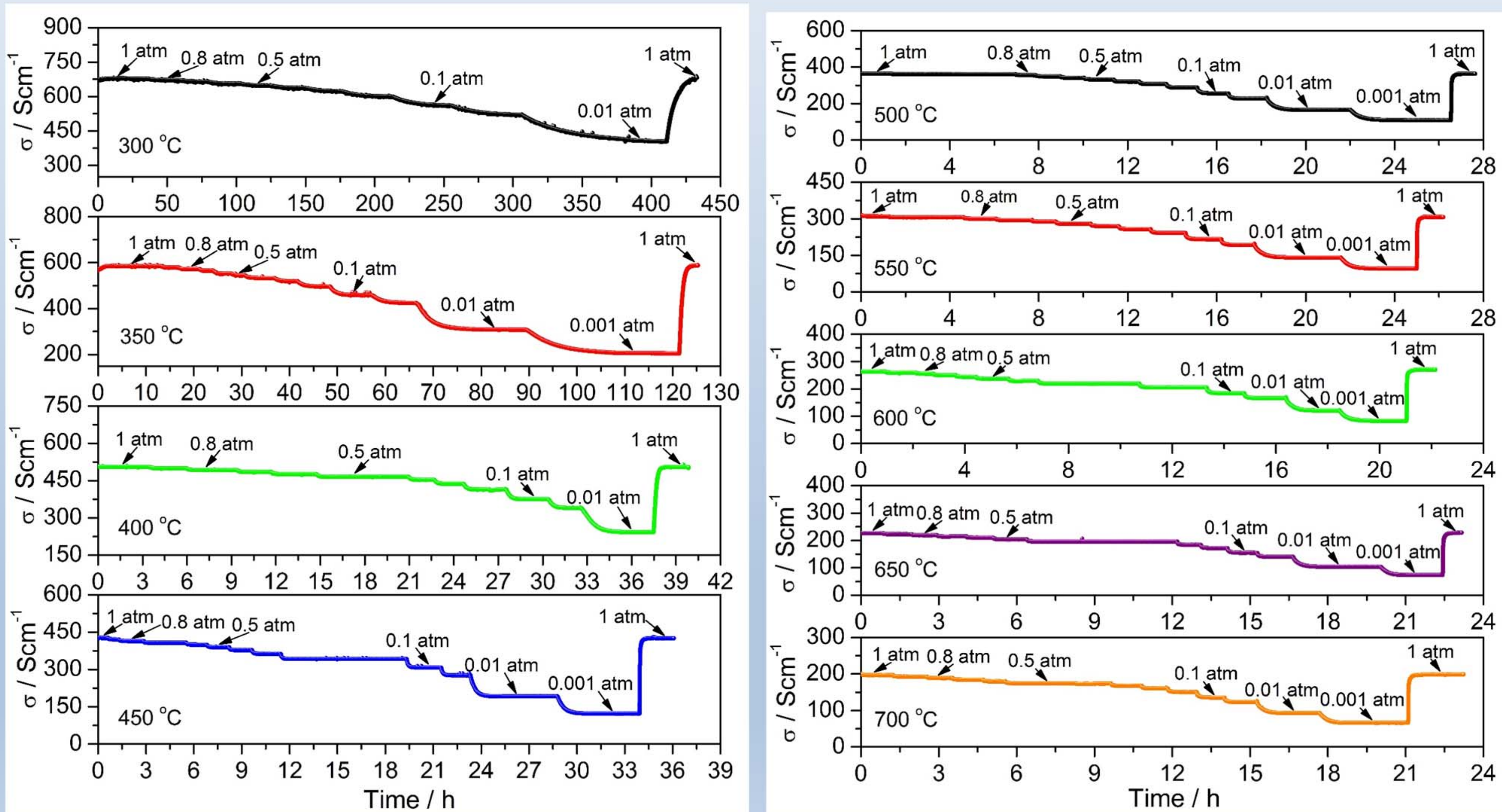




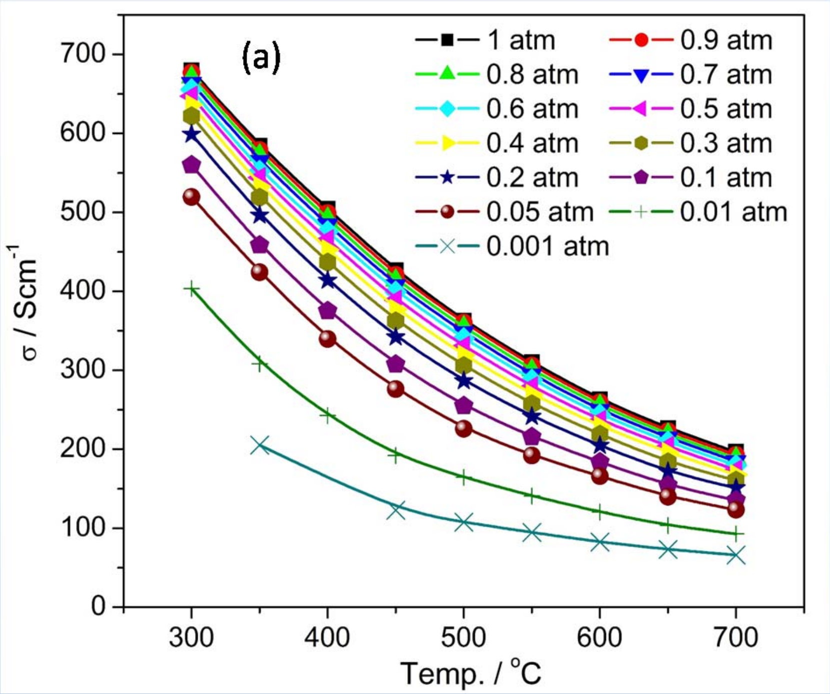
- B-site doped SCO has a higher k_{ex}-value than A-site doped SCO
- For B-site doping, Nb>Fe
- For A-site doping, La>Y
- SCO based cathodes are 2 orders of magnitude higher k_{ex} value than LSCF

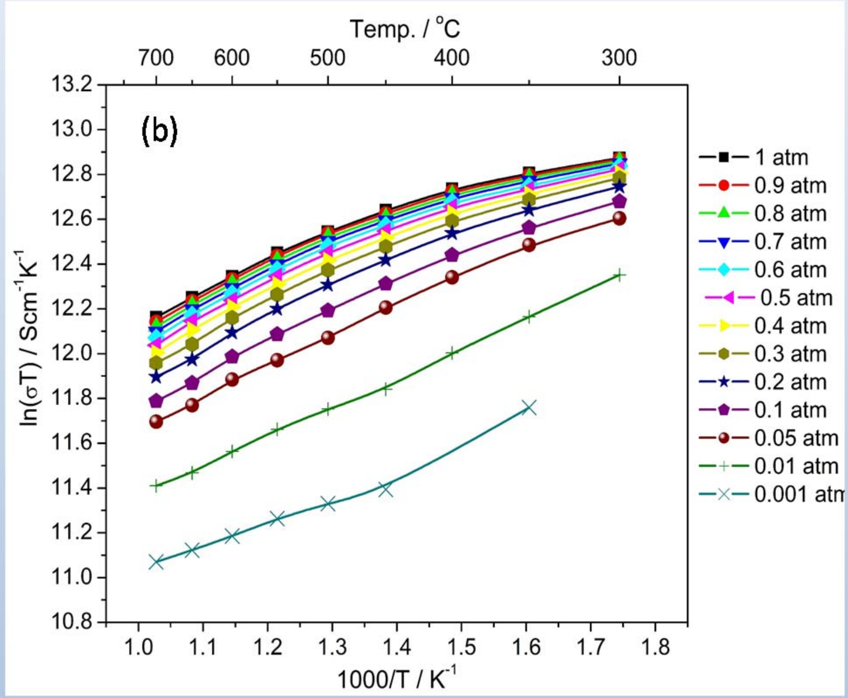
Journal of the Electrochemical Society*, 10.1149/2.0211609jes*

σ-T-Po$_2$ Data of Nb-SrCoO$_{2.5+\delta}$



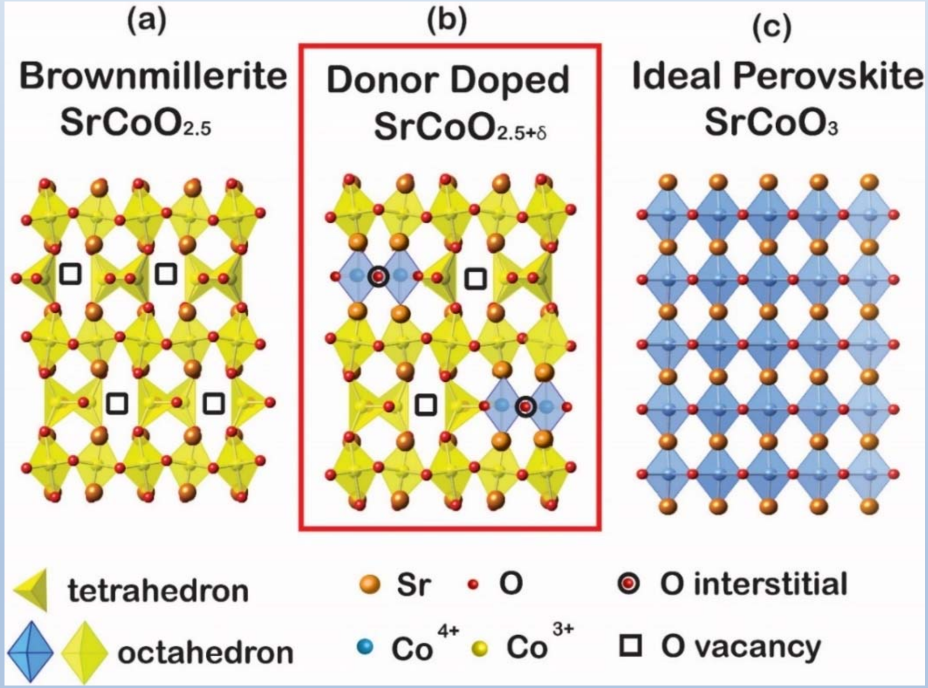
σ-T-Po_2 Data of Nb-$SrCoO_{2.5+\delta}$





- *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:

$$\frac{1}{2}O_2(g) + 2Co_{Co}^{X} + V_I^{X} \rightleftarrows O_I'' + 2Co_{Co}^{\cdot} \qquad K_{ox} = \frac{[O_I''][Co_{Co}^{\cdot}]^2}{P_{O_2}^{0.5}[Co_{Co}^{X}]^2[V_I^{X}]}$$

Disproportionation reaction:

$$2Co_{Co}^{X} \rightleftharpoons Co_{Co}^{\cdot} + Co_{Co}' \qquad K_{dsp} = \frac{[Co_{Co}^{\cdot}]\cdot[Co_{Co}']}{[Co_{Co}^{X}]^2}$$

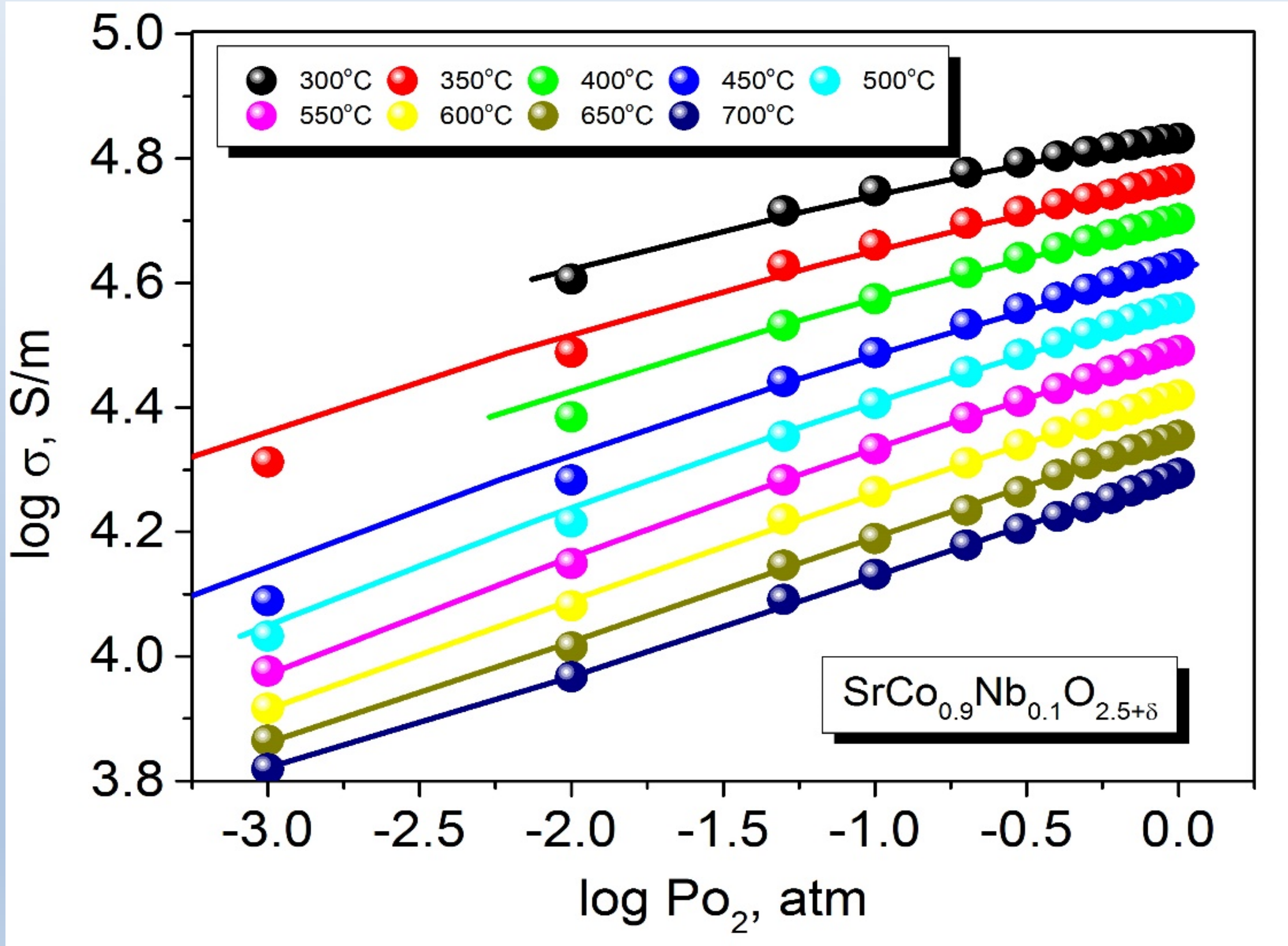
Charge neutrality: $2[Nb_{Co}^{\cdot\cdot}] + [Co_{Co}^{\cdot}] = 2[O_I''] + [Co_{Co}']$

Co-site conservation: $[Co_{Co}^{X}] + [Co_{Co}^{\cdot}] + [Co_{Co}'] + [Nb_{Co}^{\cdot\cdot}] = 1$

Oxygen-site conservation: $[V_I^{X}] + [O_I''] = 0.5$

Electron-hole conductivity: $\sigma = [Co_{Co}^{\cdot}]c_0F\mu; \;\; \mu = \frac{e\tau}{m*}$

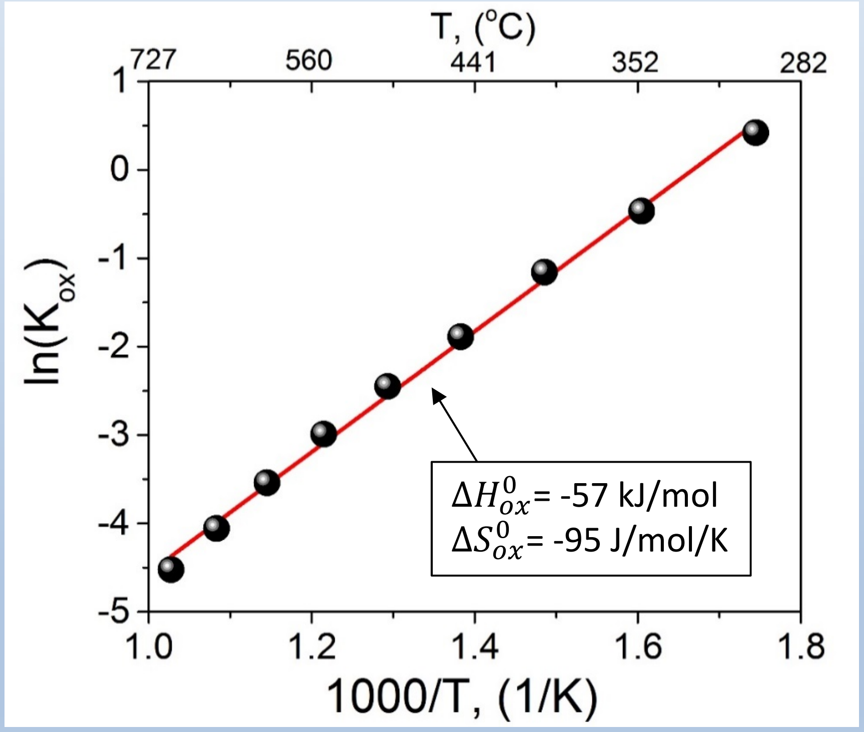
Experimental *vs* Modeled

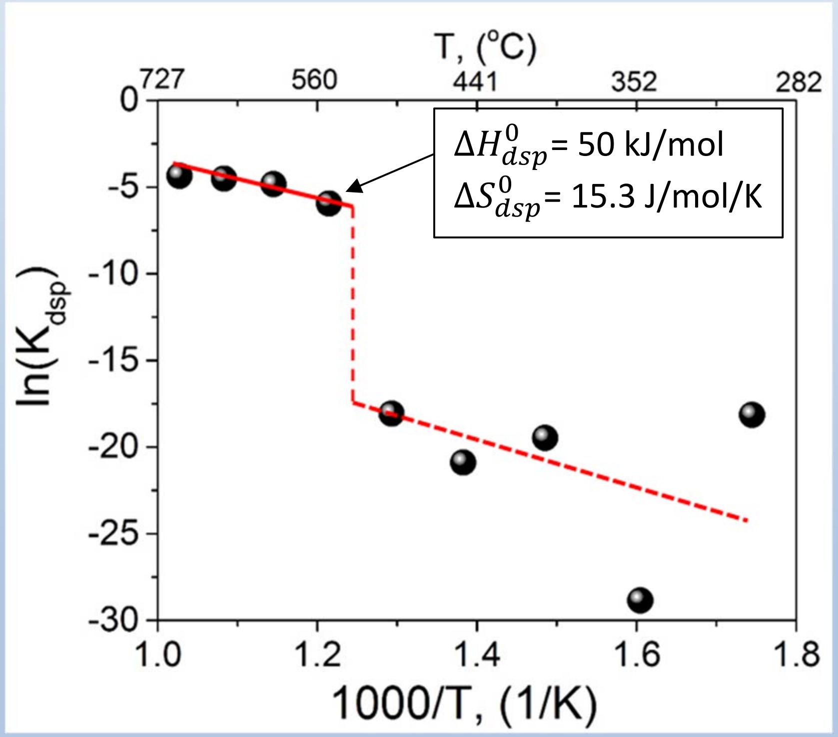


Equilibrium Constants of Defect Reactions

$$\frac{1}{2}O_2(g) + 2Co_{Co}^{\times} + V_I^{\times} \rightleftharpoons O_I'' + 2Co_{Co}^{\cdot}$$

$$2Co_{Co}^{\times} \rightleftharpoons Co_{Co}^{\cdot} + Co_{Co}'$$

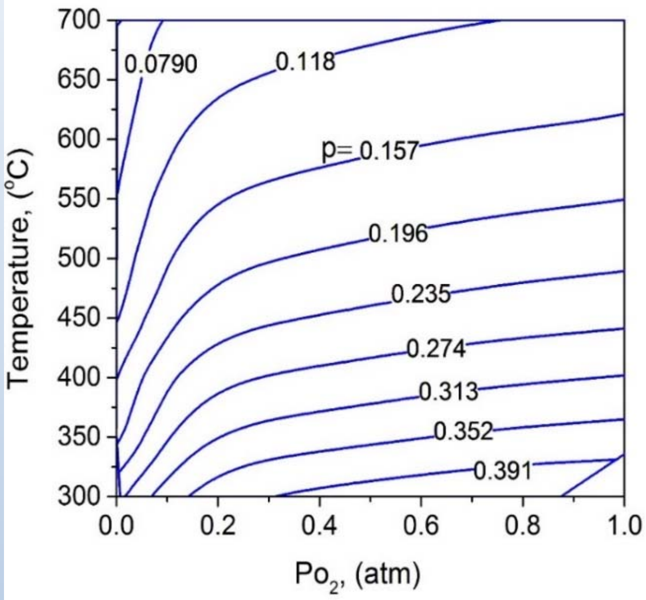


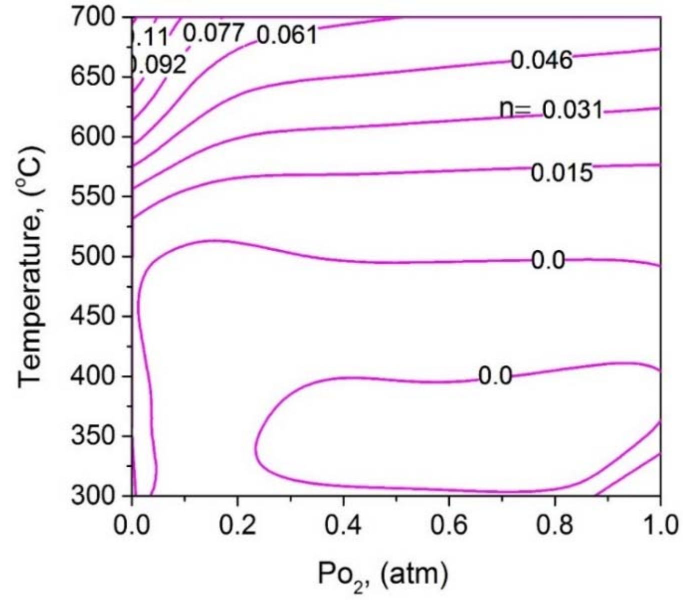


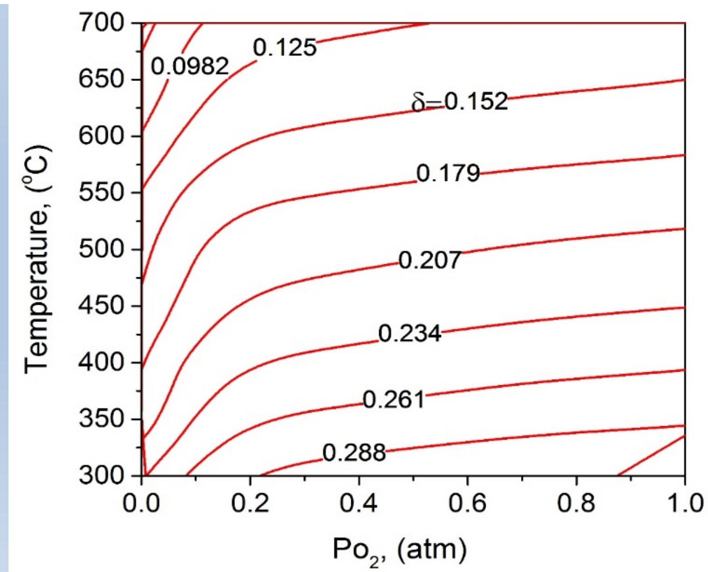
$$-\frac{\Delta H^0_{ox}}{RT} + \frac{\Delta S^0_{ox}}{R} = lnK_{ox}$$

$$-\frac{\Delta H^0_{dsp}}{RT} + \frac{\Delta S^0_{dsp}}{R} = lnK_{dsp}$$

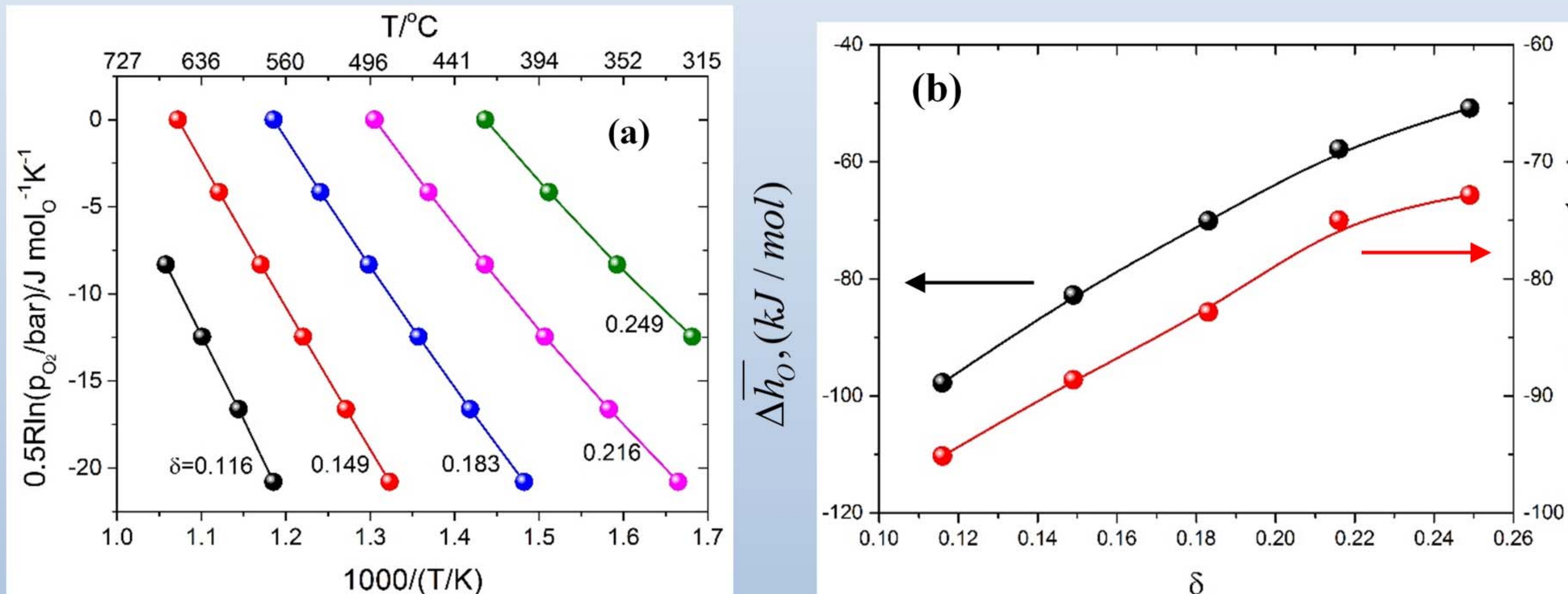
Concentration Contours of Nb-$SrCoO_{2.5+\delta}$





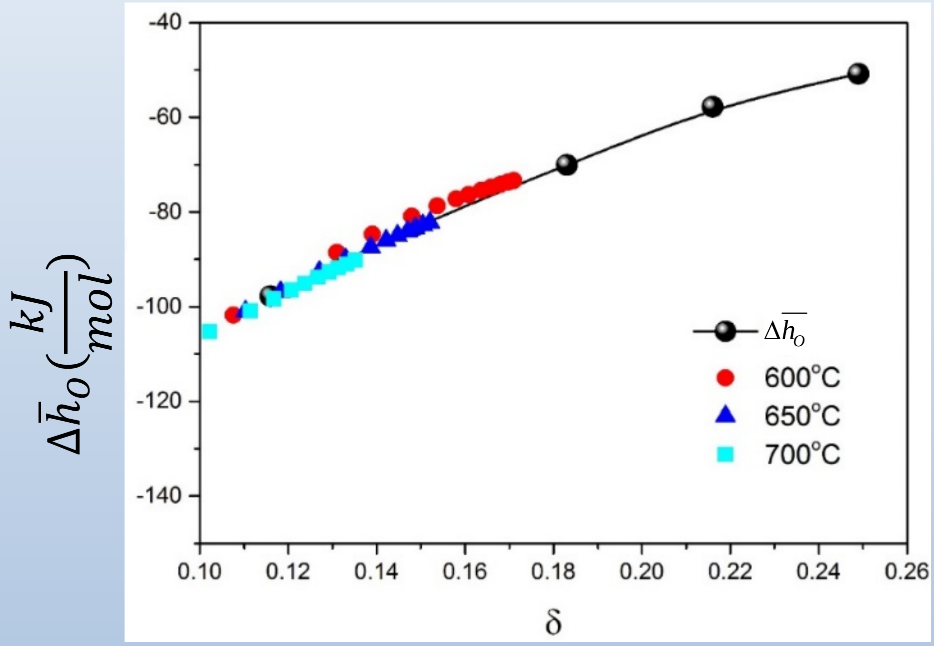


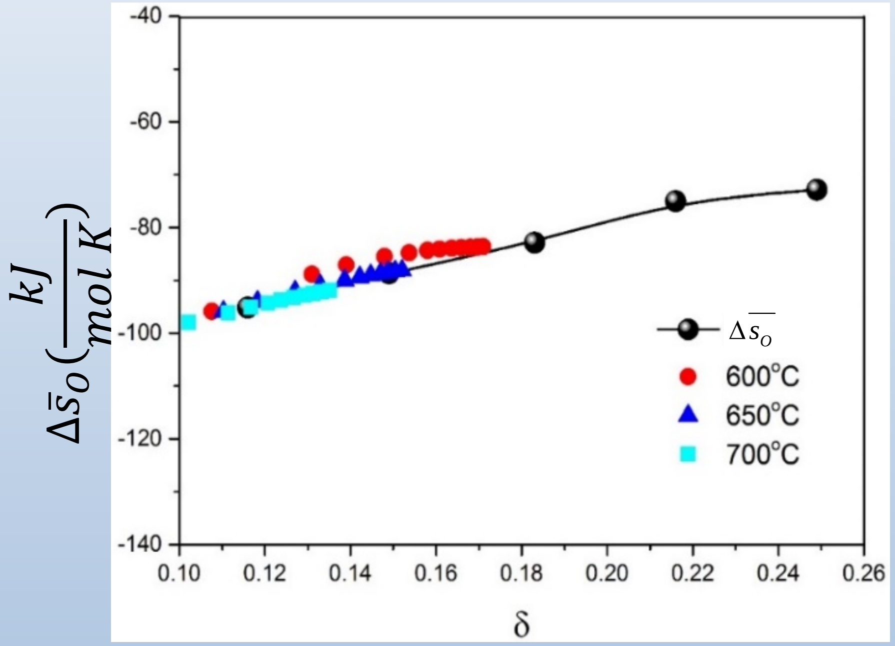
Thermodynamic Properties of Nb-$SrCoO_{2.5+\delta}$



$$\frac{R}{2} ln p_{O_2} = \frac{\Delta\overline{h_O}}{T} - \Delta\overline{s_O}$$

Partial Molar *vs* Integral Molar Properties

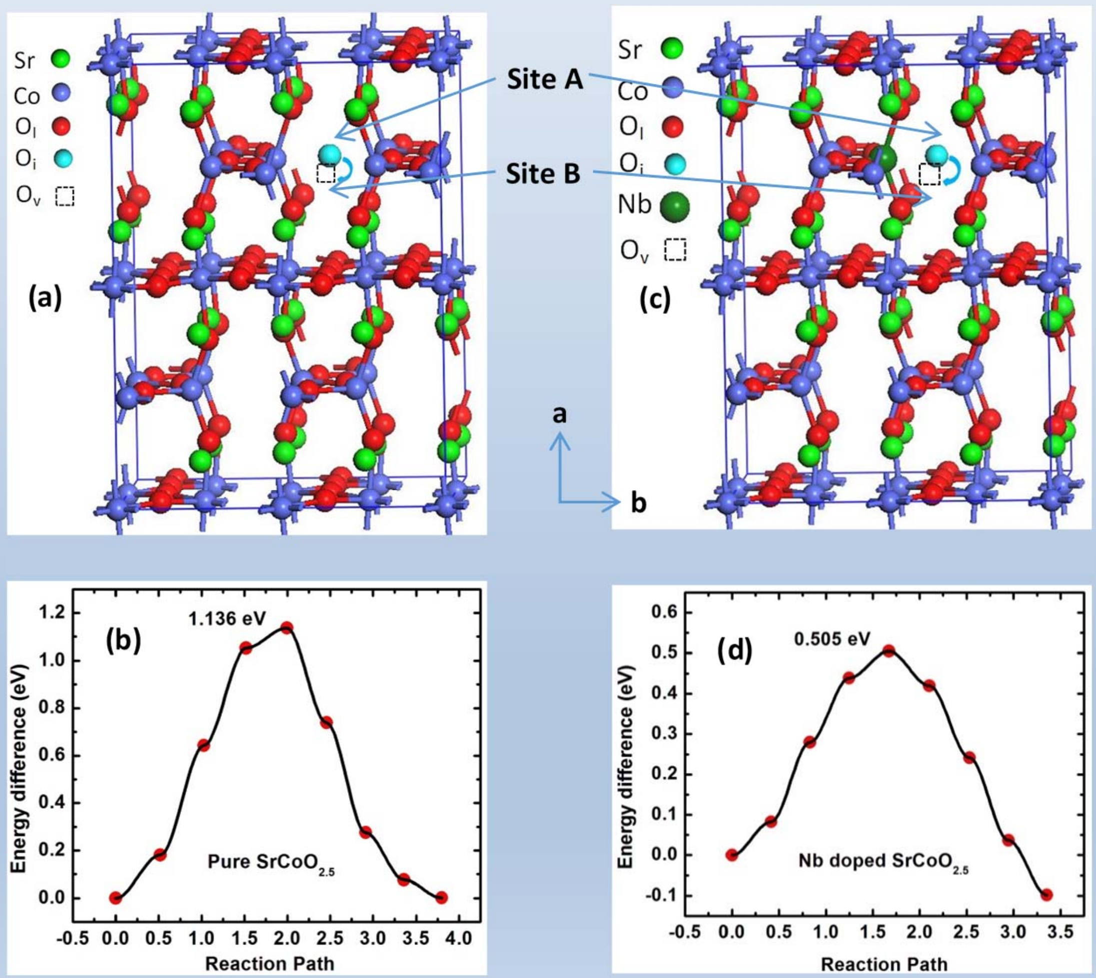




$$\Delta\overline{h_0} = \frac{\partial[Co'_{Co}]}{\partial\delta}\Delta H^0_{dsp} + \Delta H^0_{ox}$$

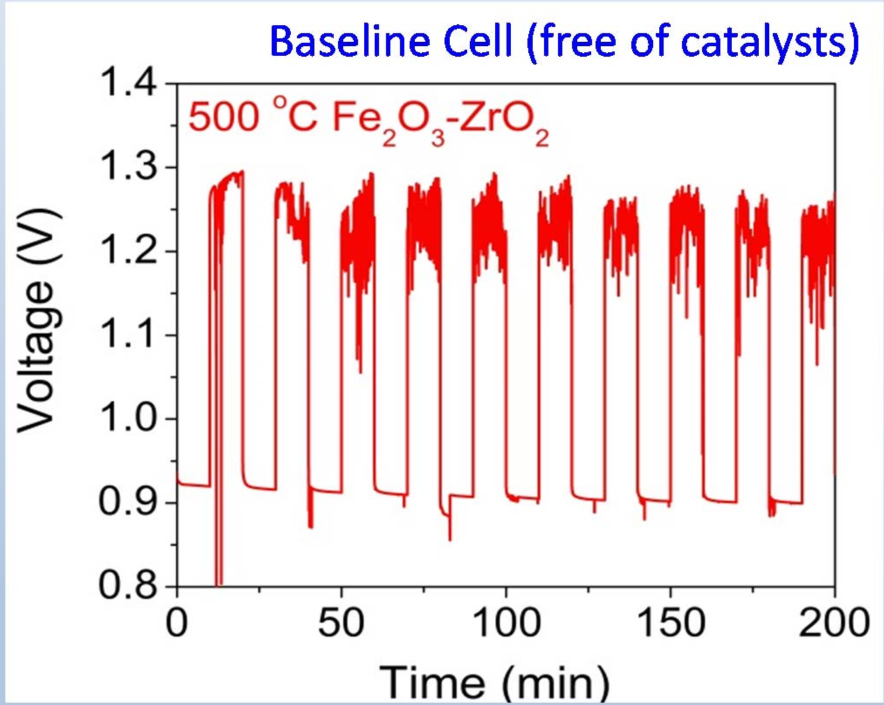
$$\Delta\overline{s_0} = \frac{\partial[Co'_{Co}]}{\partial\delta}\Delta S^0_{dsp} + \Delta S^0_{ox} + s_0(conf)$$

DFT Calculations Supporting the Formation of Oxygen Interstitials



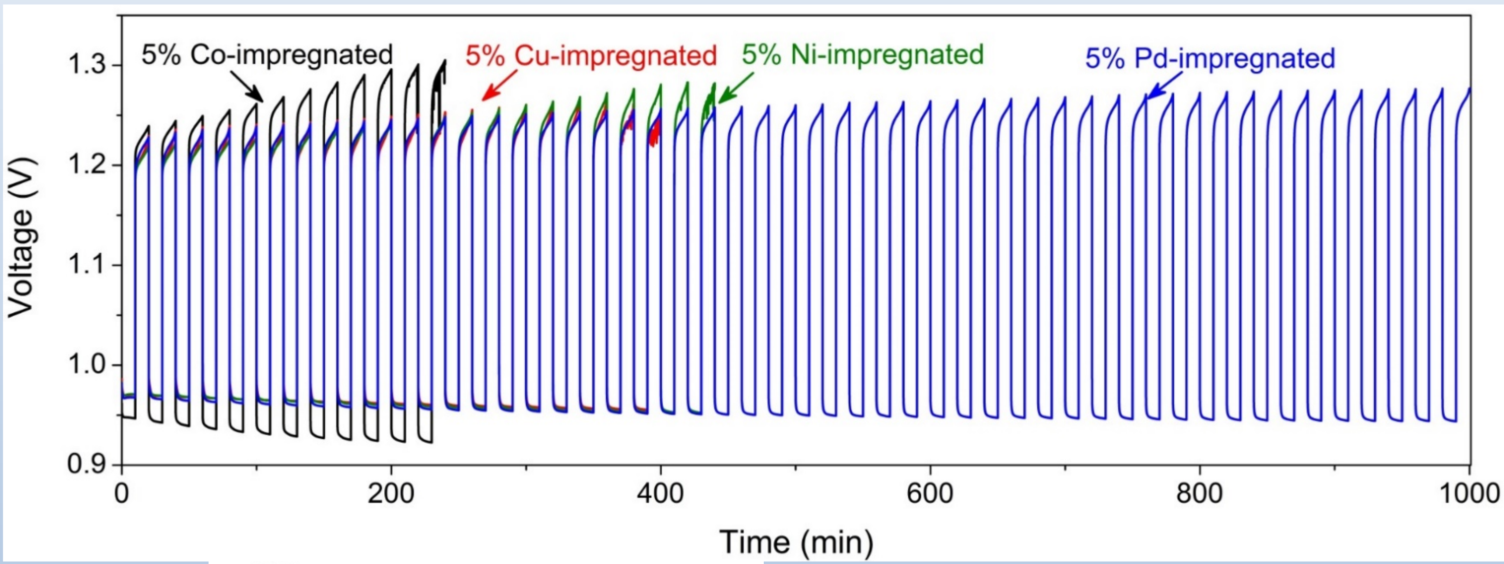
Evaluations of Button Cell Performance

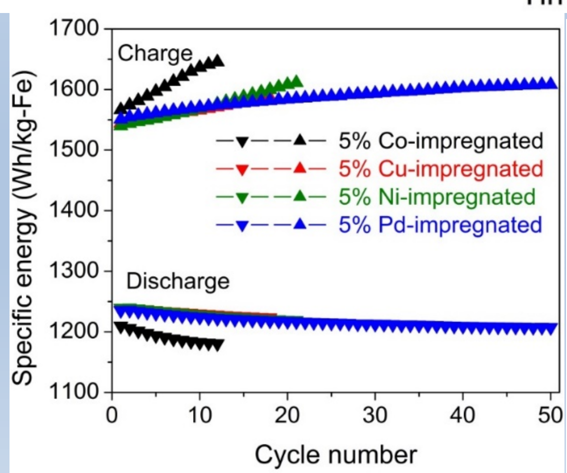
- Fe loading : 0.056 g
- Discharge/charge current:
  - C/5.5: 12.7 mA (10 mA cm^{-2})
  - C/5: 14 mA (11 mA cm^{-2})
  - C/3: 23.4 mA (18.5 mA cm^{-2})
  - 1C: 70. 1 mA (55.3 mA cm^{-2})
- Depth of discharge (DoD) at 20%
  - 1 h @ C/5
  - 36 min @ C/3
  - 12 min @ 1C

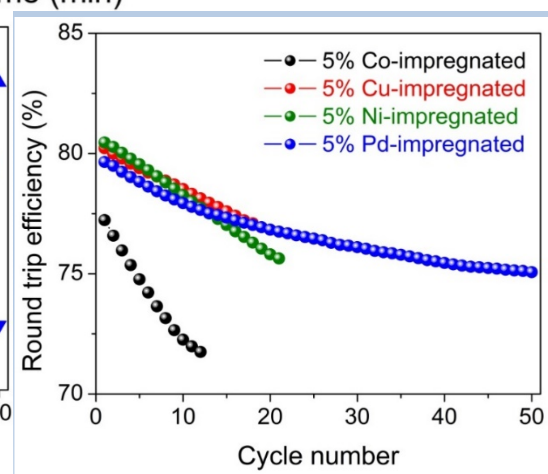


The Effect of Fe-Bed Catalysts on Battery Performance

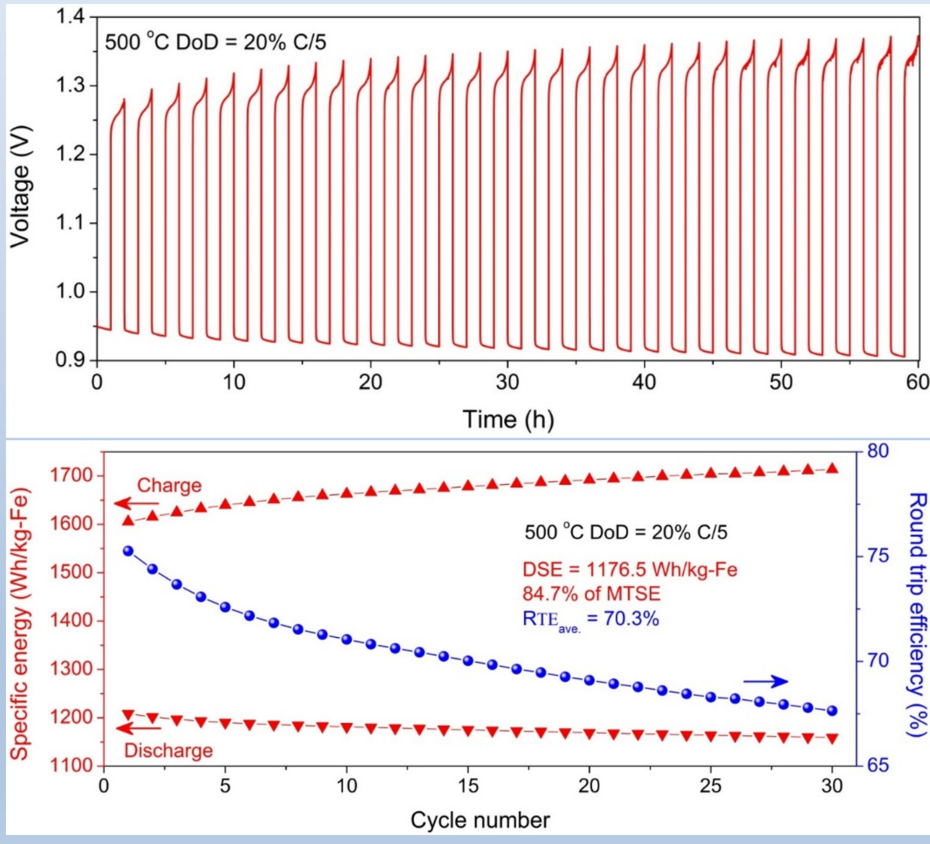
500 ^{o}C; 10 mA cm^{2} (C/5.5); 10 min discharge/charge; DoD=3%





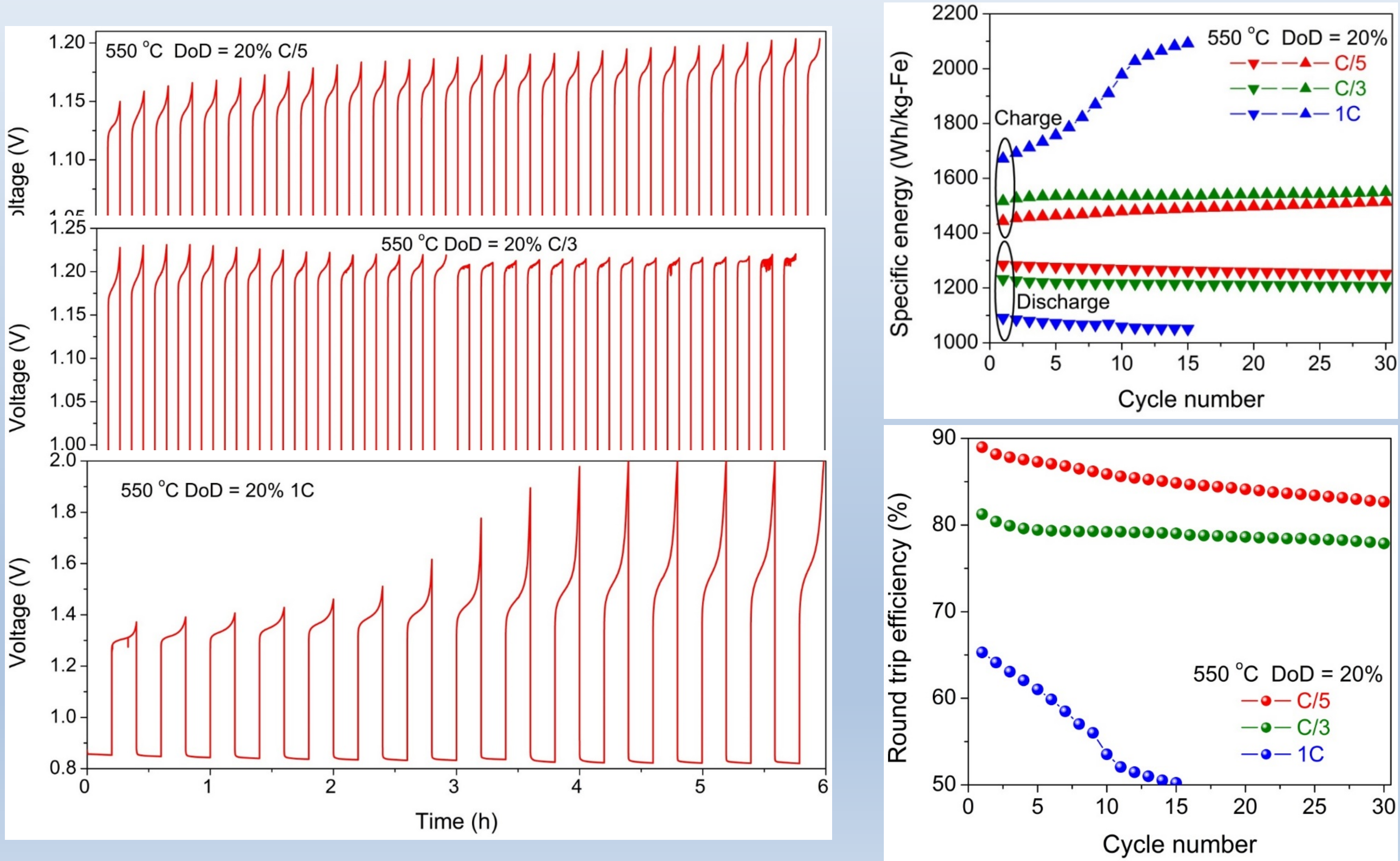


Evaluations at Higher DoD (Fe-Utilization)



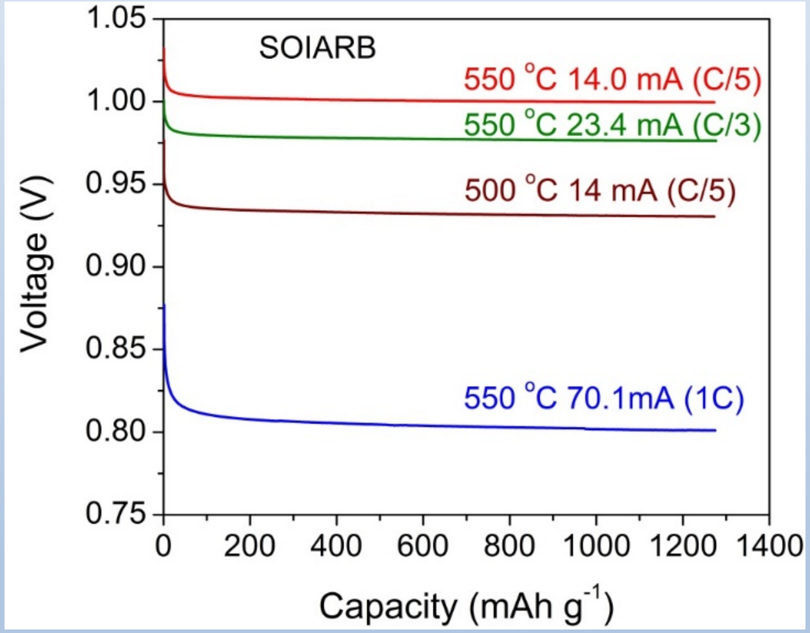
- 5wt% Pd-impregnated Fe_2O_3-ZrO_2
- Tested at 500^{o}C
- Rate: 0.2C (11 mA/cm^2 or 250 mA/g)
- DoD=20%
- Charge/discharge duration: 1 hour
- Fe-loading: 0.056 grams

The Evaluation at Different C-rates

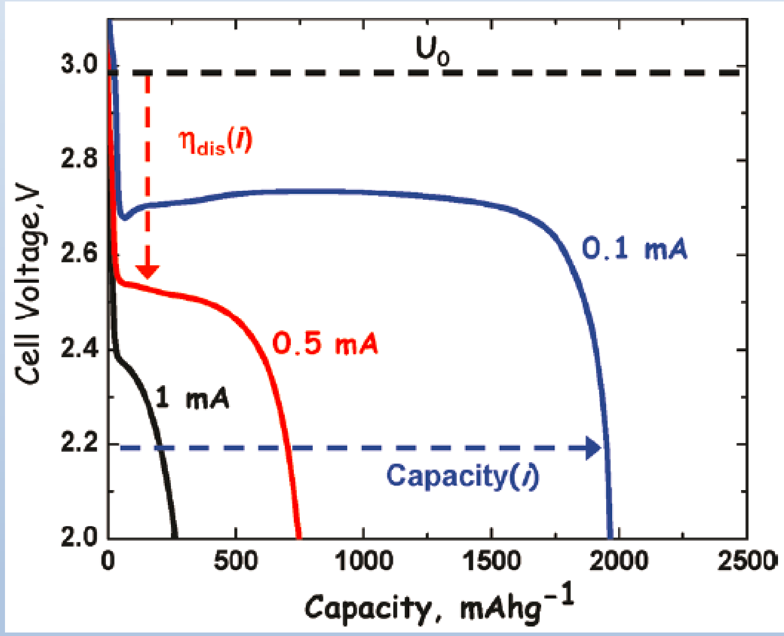


Comparison with Li-O_2 Battery

SOMARB

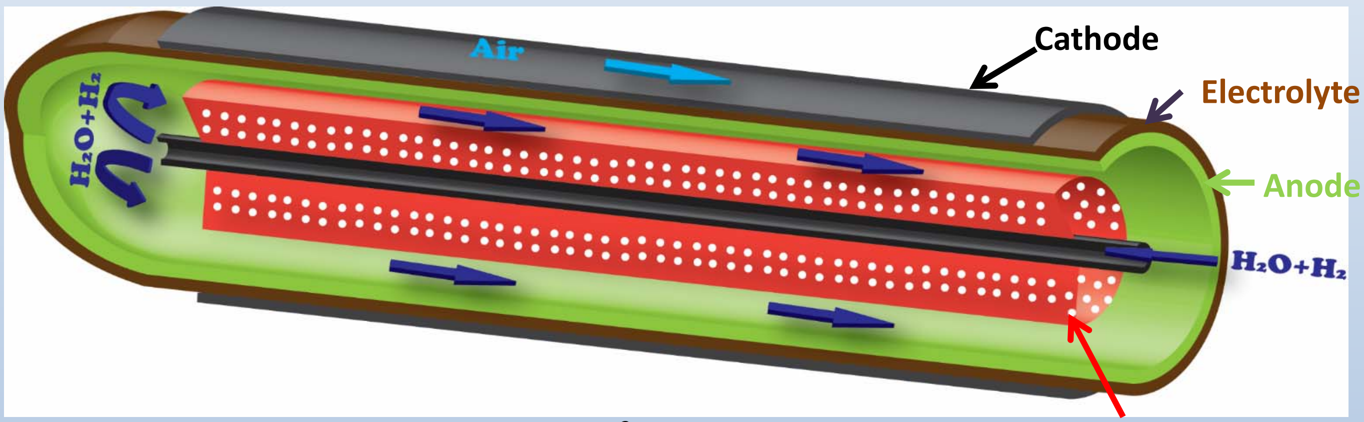


Li-O_2 battery



P. Adelhelm, et al. Beilstein J. Nanotechnol., 2015, 6, 1016; G. Girishkumar, et al. J Phys. Chem. Lett., 2010, 1, 2193.

A Fe-Bed Installed Commercial Scale SOFC



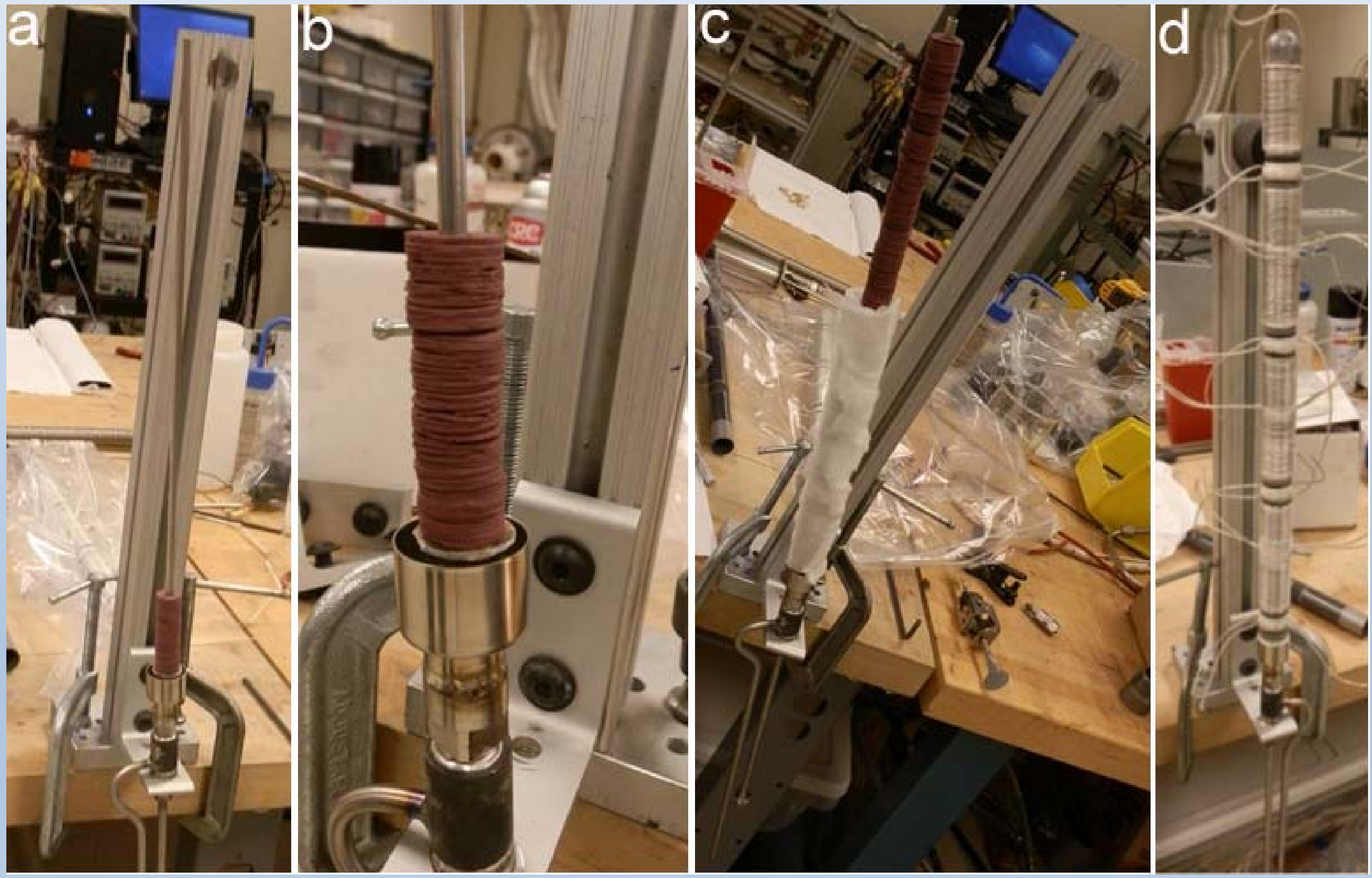
Cathode reaction: $O_2 + 4e' = 2O^{2-}$

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

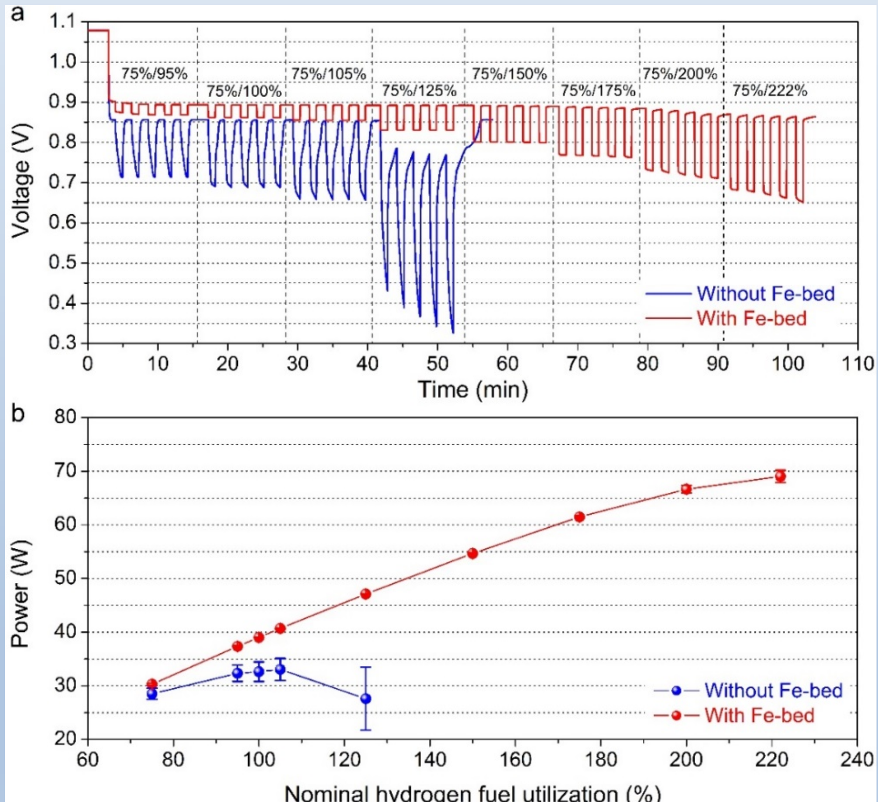
$\uparrow \qquad \downarrow$

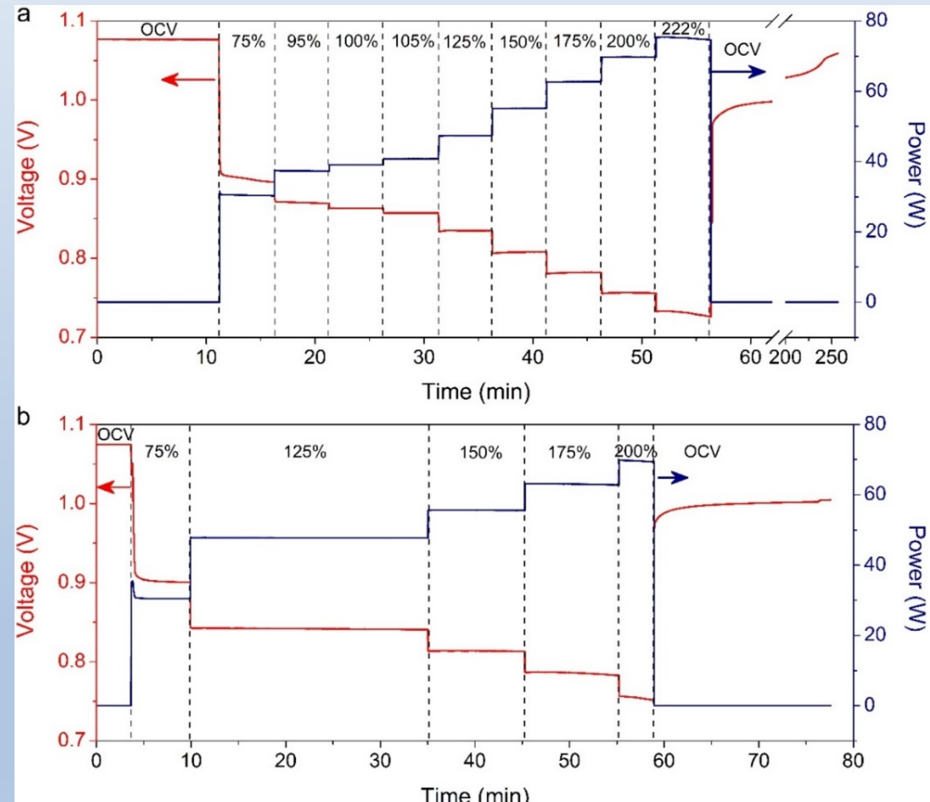
Fe-bed: $H_2 + FeO \leftarrow Fe + H_2O$

Installation of Fe-bed into Pilot-scale Cell at Atrex Energy

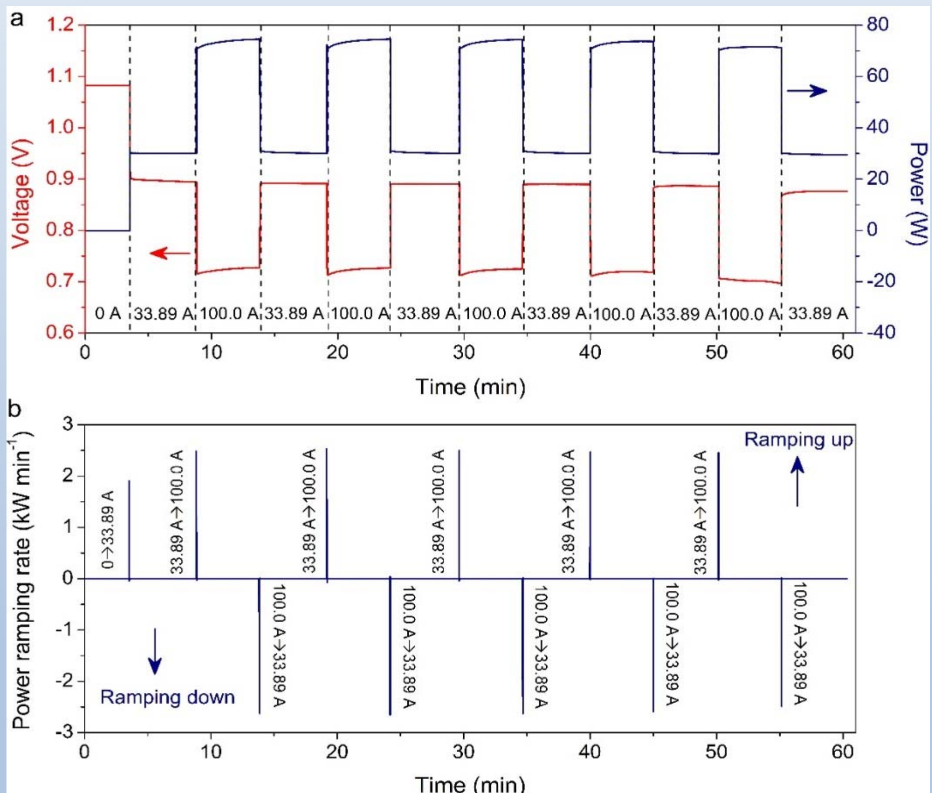


Overload Tolerance Capability (Current cycling with constant H_2 flow)



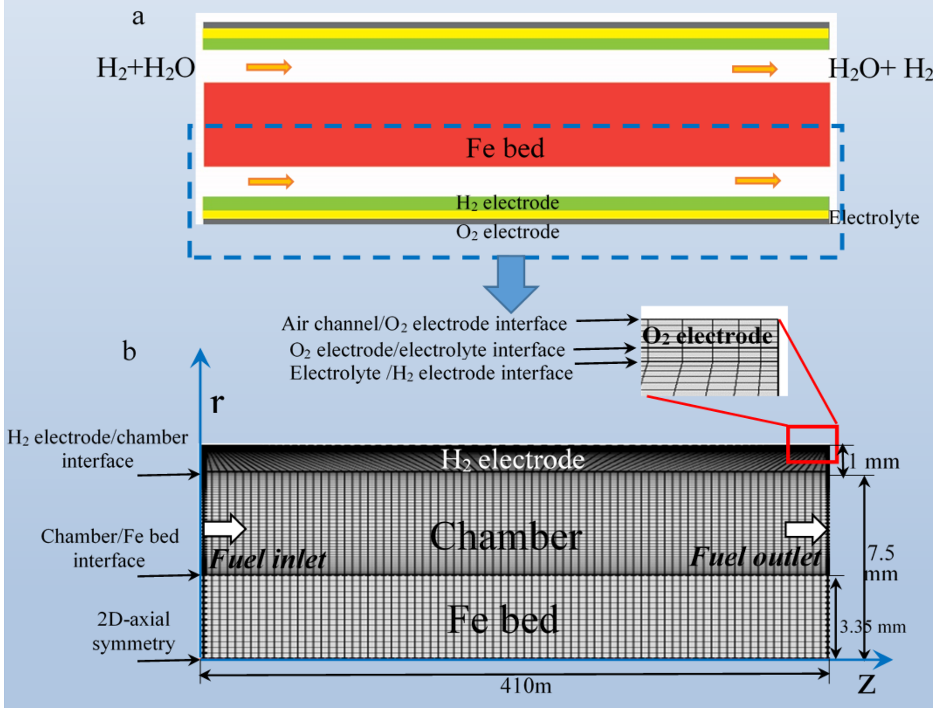


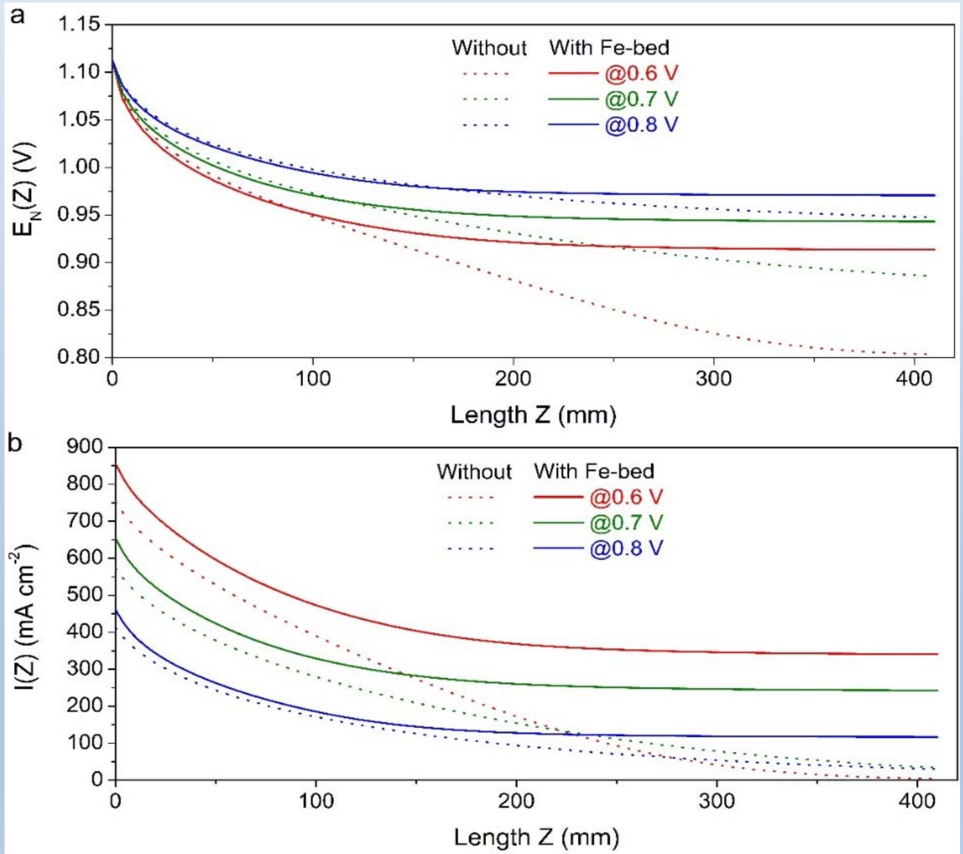
Fast Ramping Power Capability



- 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_3O_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

Acknowledgement

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