Determination of overpotential characteristics of reversible solid oxide cells via impedance spectroscopy and correlation with cell degradation

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Publication date:
2011

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Citation (APA):

Graves, C. R. (Author), Ebbesen, S. D. (Author), & Hjelm, J. (Author). (2011). Determination of overpotential characteristics of reversible solid oxide cells via impedance spectroscopy and correlation with cell degradation. Sound/Visual production (digital)

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Determination of overpotential characteristics of reversible solid oxide cells via impedance spectroscopy

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Oct. 11th, 2011

220th ECS Meeting

Boston, MA

Risø DTU

National Laboratory for Sustainable Energy

Outline

- Introduction + Purpose
- Experimental
- Results + Modeling
- Applications
- Conclusions

Introduction + Purpose

- Solid oxide cells promise economical + efficient sustainable energy conversion

Introduction + Purpose

Economical energy storage is ultimately needed to scale up renewable energy to meet a significant fraction of demand

High temp. co-electrolysis of $\text{H}_2\text{O} + \text{CO}_2$

- makes very efficient use of electricity + heat (near-100% electricity-to-syngas efficiency)
- provides high reaction rates
- directly produces syngas (CO/H_2 mixture) for use in conventional catalytic fuel synthesis reactors.

[C. Graves, S.D. Ebbesen, M. Mogensen, K.S. Lackner, *Renewable and Sustainable Energy Reviews* 15 (2011) 1-23]

Electrolysis cells

Intermittent electricity → hydrocarbon fuels

Reversible fuel cells

Intermittent electricity → hydrocarbon fuels + on-demand electricity

Introduction + Purpose

Solid oxide cells

- High performance for reversible reactions
 - Oxidation of $\text{H}_2/\text{CO}/\text{CH}_4$
 - Reduction of $\text{H}_2\text{O}/\text{CO}_2$
- Important goal is improving long-term durability

From: **Graves C**, Ebbesen SD, and Mogensen M, "Co-electrolysis of CO_2 and H_2O in Solid Oxide Cells: Performance and Durability," *Solid State Ionics* 192(1): p. 398-403 (2011).

Importance of current density

Fuel production economics is promising...

- Re. choice of "safe" and "harsh" current densities:
- *Graves, Ebbesen, Mogensen 2010*
doi: 10.1016/j.ssi.2010.06.014
 - *Xiufu Sun's talk tomorrow*
 - *Knibbe, Traulsen, Hauch, Ebbesen, Mogensen 2010*
doi: 10.1149/1.3447752
 - *Ebbesen, Graves, Hauch, Jensen, Mogensen 2010*
doi: 10.1149/1.3464804
 - *Ebbesen & Mogensen 2010, doi: 10.1149/1.3455882*

Importance of current density & capacity factor

Introduction + Purpose

Degradation of cell components is related to voltage across each component

- Fuel cell mode: too high anodic overpotential for Ni $\rightarrow$ NiO
- Electrolysis mode: too high anodic overpotential for oxygen electrode $\rightarrow$ microstructural degradation at interface with electrolyte

Normally, measuring overpotentials requires a reference electrode

- Here we demonstrate calculation of component-wise overpotentials (e.g. across each electrode and the electrolyte) for fuel cell + electrolysis polarization
 - without using a reference electrode
 - by careful measurement + analysis of impedance data
 - Also facilitates study of electrode kinetics

See also recent work by Leonide and coworkers:

Leonide A, Apel Y, and Ivers-Tiffée E, ECS Transactions, (2009). 19(20): 81-109.

A. Leonide et al., Journal of Power Sources, (2011). 196(17): 7343-7346.

Experimental

- Test set-up similar to
- Cell type:
 - Most measurements on Ni-YSZ/YSZ/CGO/LSC (16 cm²)
 - LSC oxygen electrode chosen because its impedance response has less overlap with other impedance processes (facilitates fitting impedance data)
- Test conditions: (impedance data measured at)
 - 650 – 850 °C
 - Varying H₂/CO/H₂O/CO₂ compositions to fuel electrode and pO_2 to ox. electrode
 - Varying current density

From: Ebbesen SD, **Graves C**, and Mogensen M, Production of Synthetic Fuels by Co-Electrolysis of Steam and Carbon Dioxide. International Journal of Green Energy, (2009). 6(6): p. 646 – 660.

Results

- Fuel cell mode – impedance measured under polarization

750 °C,
 $H_2/H_2O=97/3$,
 ox.el.=air

Results

- Reversible – impedance measured under polarization

Results

- Impedance measured under polarization

R_S is affected by temperature changes e.g. heating especially during fuel cell polarization

Using electrolyte conductivity activation energy of 0.8-0.9 eV for R_S , ΔT accounts for ΔR_S , approximately (calculated ΔT is slightly higher than measured ΔT ; thermocouple is ~1mm from electrolyte which can account for this)

Results

- Those were “fixed oven temperature” measurements
- The heating/cooling upon polarization effects temperature activated processes e.g. electrode kinetics
- This effect can be compensated for by using R_S as a temperature indicator and adjusting the oven temperature at each load setting, to obtain “fixed cell temperature” (fixed R_S) measurements:

750 °C,
 $\text{H}_2/\text{H}_2\text{O}=97/3$,
ox.el=air

Modeling the impedance data

- To quantify resistance contributions from each cell component, the impedance data must be carefully modeled
- Equivalent circuits or models based on chemical/physical processes
- Today all results used an equivalent circuit based on a previous equivalent circuit model established for Ni-YSZ/YSZ/LSM-YSZ type cells, now with a Gerischer element for oxygen electrode; we are also fitting to a model without circuit elements
- The low-frequency inductive loop observed at high current densities/overpotentials in both fuel cell & electrolysis modes has been speculated as various adsorption/surface layer processes. It affects quantifying the gas concentration process and should be included in the model

Modeling the impedance data

- Co-electrolysis – impedance measured under polarization

800 °C,
co-electrolysis
90%-reactants
($\text{CO}_2 + \text{H}_2\text{O}$),
ox.el. = O_2

Modeling the impedance data

- Co-electrolysis – impedance measured under polarization

Break down of cell resistance

800 °C,
co-electrolysis
90%-reactants
($\text{CO}_2 + \text{H}_2\text{O}$),
ox.el. = O_2

Calculating overpotential curves from fitted data

Meaning of $R_{X,EIS}$ vs i

$R_{EIS} = dU/di$ (local slope of an i - U curve)

To recreate an i - U curve, $dU = R_{EIS} \cdot di$, so integrate,
or numerically each $U_n = U_{n-1} + R_{EIS,n} \cdot (i_n - i_{n-1})$

Since we have a limited number of data points, use a fit (spline) to i - R curves

What does it look like? Examples

Break down of overpotentials

800 °C,
co-electrolysis
90%-reactants
($\text{CO}_2 + \text{H}_2\text{O}$),
ox.el. = O_2

Added to OCV to obtain
calculated i - U curve

Calculating overpotential curves from fitted data

Overlaid on measured i-U curve → agreement
(it had better agree if the method works 😊)

Reversible
polarization
- asymmetry

800 °C,
 $\text{H}_2/\text{H}_2\text{O}=50/50$,
ox.el.= O_2

Further considerations

- Effect of number data points (errors that arise)
- Effect of level of detail of model (errors)

Applications

- Overpotential vs time (degradation)
- Obtaining electrode kinetics parameters
- Connecting/reconciling DC and AC measurements (shown in earlier slide)
- Determine safe operating conditions (avoiding Ni/NiO)
- Comparing with 3-electrode measurements to study ref. electrode effects

Conclusions

- Analysis method demonstrated for electrolysis + fuel cell operation
 - careful measurement + analysis of impedance data obtained on full cells
→ calculate overpotential-current curves
- Isothermal i-U measurements obtained
 - and procedure developed
 - enables more meaningful study of transport/kinetics parameters
- Method being applied to long-term durability tests to calculate overpotential across each component during testing (observe evolution of overpotentials) and correlate with cell degradation

Acknowledgements

- Xiufu Sun for some of the measurements
- Energinet.dk
- SERC.dk
- Topsoe Fuel Cell

Thank you!