Fundamental physics and chemistry of direct electrochemical oxidation in SOFC

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The MURI research seeks to understand the chemical fundamentals of DECO

Important fundamental issues
- Establish elementary kinetics of charge-transfer processes
- Establish elementary kinetics of internal reforming and partial oxidation
- Couple elementary thermal chemistry and electrochemistry
- Determine the chemical routes to deposit formation
- Bridge scales (atomic to fluid flow) to predict cell-level performance

Technical approach
- Develop and apply predictive models across length scales
- Devise and operate experiments that illuminate particular processes
- Use focused experiments to inform, guide, and validate modeling
- Use modeling to help focus and interpret experimentation

Overall objectives
- Develop and validate advanced modeling tools
- Assist the optimal design and development of fuel-cell architectures
Concerted theory and experimentation work to improve understanding the fundamentals

Model across length scales

Experiments to isolate physics

Innovative new materials
Molecular dynamics assists understanding surface chemistry and transport.

OH(s) + OH(s) → H2O(g) + O(s)

$E_a \approx 90 \text{ kJ/mol}$

Hydrogen coverage of YSZ
Surface diffusivities are derived from molecular-dynamics simulations.

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Diffusivity of H on YSZ

\[ T = 1000 \, ^\circ\text{C} \]
\[ D = 6.28 \times 10^{-6} \, \text{cm}^2/\text{s} \]
Pattern anodes are an important vehicle to establish the charge-transfer chemistry.

Electrochemical performance:
- Voltage-current characterization
- Impedance spectroscopy
- Surface interrogation
- Micro-Raman spectroscopy
Pattern anode experiments provide polarization and impedance data.
Deposit formation affects pattern-anode cell performance significantly

Butane on pattern Ni
- Transient performance
- Surface carbon buildup
- Expands onto electrolyte

Carbon improves performance

[Graph showing voltage corrected for bulk IR losses versus current, with data points for dry H₂ initially, n-C₄H₁₀ after 4 hrs., and H₂ after 32 hrs.]

Ar:fuel 2:1
T = 850°C
Pattern 100 μm

[Image of carbon deposits on Ni]
UMCP’s optically accessible anode provides a means to interrogate surface chemistry.
Samaria-doped ceria (SDC15) is characterized with impedance spectroscopy.

Oxidizing environment: Ar/O₂
Reducing environment: Ar/H₂/H₂O
Hydrogen electro-oxidation appears to occur on the ceria surface

\[ \text{H}_2 + \text{O}^= \rightleftharpoons \text{H}_2\text{O} + 2\text{e}^- \]

- Independent of metal
  - Reaction on ceria surface
- Activation energy matches
  - \( \sigma_{\text{electronic}} = 2.31 \pm 0.02 \text{ eV} \)
- Rate-limiting step
  - electron migration

\[ \sigma_{\text{electrode}} = \sigma_{\text{cl}}^0 X P_{\text{O}_2}^{-1/4} \]
MD simulations reveal the role of different metals in catalyzing carbon growth

Initial configuration:
- 5 $\text{C}_{20}$ monocyclic rings,
- 10 $\text{C}_{4}$ acyclic chains
- 15 metal atoms

QM: Hybrid DFT functional B3LYP
MD: ReaxFF reactive force fields

Homogeneous chemistry models predict observed fuel conversion and deposits.
Gas-phase kinetics transforms the fuel as a function of composition and residence time.
Molecular-weight chemistry is a perturbation on heterogeneous and electrochemistry.

Solve dual-channel model
- Neglect gas-phase chemistry
- Simple gas-phase chemistry
- Include heterogeneous chemistry
- Include electrochemistry

Evaluate fluxes to/from channel

Elementary gas-phase chemistry
- Modified plug flow
- Imposed wall fluxes
- Predict molecular-weight growth

Large mechanism
- ~ 2500 reactions
- ~ 300 species

Combustion
- Soot models
Cell structure and operation affect the gas-phase molecular-weight growth

Inlet composition
- 49% CH₄, 50% H₂O
- 1% C₂H₆, trace C₃H₈, C₄H₁₀

Flow conditions
- T = 800 °C, p = 1 atm
- V = 20 cm/s

Geometry
- 1 mm X 1 mm channel

Charge transfer via H₂
The models incorporate elementary charge-transfer chemistry

Nickel surface reactions
- $\text{H}_2 + (\text{ni}) + (\text{ni}) \leftrightarrow \text{H(ni)} + \text{H(ni)}$
- $\text{H}_2\text{O} + (\text{ni}) + (\text{ni}) \leftrightarrow \text{OH(ni)} + \text{H(ni)}$
- $\text{OH(ni)} + \text{H(ni)} \leftrightarrow \text{O(ni)} + \text{H}_2 + (\text{ni})$

Triple-phase charge exchange
- $\text{H(ni)} + \text{O(s)} \leftrightarrow (\text{ni}) + \text{e}^- + \text{OH(s)}$
- $\text{H(ni)} + \text{OH(s)} \leftrightarrow (\text{ni}) + \text{H}_2\text{O(s)} + \text{e}^-$

YSZ surface reactions
- $\text{VO(s)} + \text{Ox} \leftrightarrow \text{VO} + \text{O(s)}$
- $\text{H}_2\text{O(s)} \leftrightarrow \text{H}_2\text{O} + \text{VO(s)}$

Surface and bulk species
- (ni) Empty Ni site
- H(ni) H adsorbed on Ni
- OH(ni) OH adsorbed on Ni
- Ox Bulk oxygen ion, charge = $-2$
- VO Bulk oxygen vacancy
- VO(s) Oxygen vacancy on YSZ
- O(s) Surface O ion, charge = $-2$
- H$_2$O(s) Surface H$_2$O
- OH(s) Surface OH, charge = $-1$
Goodwin’s pattern-anode model is the first of its kind.
Performance is predicted from elementary chemistry and thermodynamics

<table>
<thead>
<tr>
<th>Reaction</th>
<th>A</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2(g) + 2(Ni) \rightleftharpoons 2\text{H}(Ni)_2$</td>
<td>$0.4^\circ$</td>
<td>0</td>
</tr>
<tr>
<td>$\text{H}(Ni) + \text{O}''<em>\text{ad} \rightleftharpoons (Ni) + \text{OH}'</em>\text{ad} + e'$</td>
<td>$5 \times 10^{16}$</td>
<td>90</td>
</tr>
<tr>
<td>$\text{H}(Ni) + \text{OH}'_\text{ad} \rightleftharpoons (Ni) + \text{H}<em>2\text{O}</em>\text{ad} + e'$</td>
<td>$5 \times 10^{15}$</td>
<td>90</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}(g) + (s) \rightleftharpoons \text{H}<em>2\text{O}</em>\text{ad}$</td>
<td>$1.0^\circ$</td>
<td>0</td>
</tr>
<tr>
<td>$\text{O}<em>x + (s) \rightleftharpoons \text{V}</em>\text{O}'' + \text{O}''_\text{ad}$</td>
<td>$5 \times 10^8$</td>
<td>0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Species</th>
<th>$h^0$ (kJ/mol)</th>
<th>$s^0$ (J/mol/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2(g)$</td>
<td>24.4</td>
<td>169.8</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}(g)$</td>
<td>-210.6</td>
<td>237.6</td>
</tr>
<tr>
<td>(Ni)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>H(Ni)</td>
<td>-35.81</td>
<td>36.77</td>
</tr>
<tr>
<td>O''_ad</td>
<td>-170.0</td>
<td>50.0</td>
</tr>
<tr>
<td>OH''_ad</td>
<td>-220.0</td>
<td>87.0</td>
</tr>
<tr>
<td>H$<em>2$O$</em>\text{ad}$</td>
<td>-265.0</td>
<td>98.1</td>
</tr>
<tr>
<td>O$_x$</td>
<td>-170.0</td>
<td>50.0</td>
</tr>
<tr>
<td>V''_O</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(s)</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Polarization

\[
\log (i) \text{ (mA/cm}^2) = 2
\]

Overpotential (mV)

Impedance

\[
\eta = 0 \text{ mV}
\]

\[
\eta = 70 \text{ mV}
\]
What is the role of the anode structure in promoting reforming, shifting, and CPOX
MEA models do a good job of representing measured electrochemical performance.

The Dusty-Gas model applies when the mean-free path is comparable to the pore size.

Dusty-gas model

\[ \sum_{\ell \neq k} \frac{[X_\ell]J_k - [X_k]J_\ell}{[X_T]D_{k\ell}^e} + \frac{J_k}{D_{k,Kn}^e} = -\nabla[X_k] - \frac{[X_k]}{D_{k,Kn}^e} \frac{B_g}{\mu} \nabla p \]

Effective Binary and Knudsen diffusion

\[
D_{k\ell}^e = \frac{\phi_g}{\tau_g} D_{k\ell} \quad D_{k,Kn}^e = \frac{4}{3} \frac{\tau_p \phi_g}{\tau_g} \sqrt{\frac{8RT}{\pi W_k}}
\]

Permeability (Kozeny-Carman)

\[ B_g = \frac{\phi_g^3 \tau_p^2}{72 \tau \left(1 - \phi_g\right)^2} \]

- \( J_k \): Molar flux
- \( [X_k] \): Concentration
- \( p \): Pressure
- \( \phi_g \): Porosity
- \( \tau_g \): Tortuosity
- \( \tau_p \): Pore radius
- \( d_p \): Particle diameter
The models accommodate elementary heterogeneous reforming/CPOX chemistry

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$A^*$</th>
<th>$E^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Adsorption:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. $\text{H}_2 + \text{Ni}(s) + \text{Ni}(s) \to \text{H}(s) + \text{H}(s)$</td>
<td>$1.000 \cdot 10^{-21}$</td>
<td>0.0</td>
</tr>
<tr>
<td>2. $\text{O}_2 + \text{Ni}(s) + \text{Ni}(s) \to \text{O}(s) + \text{O}(s)$</td>
<td>$1.000 \cdot 10^{-24}$</td>
<td>0.0</td>
</tr>
<tr>
<td>3. $\text{CH}_4 + \text{Ni}(s) \to \text{CH}_4(s)$</td>
<td>$8.000 \cdot 10^{-31}$</td>
<td>0.0</td>
</tr>
<tr>
<td>4. $\text{H}_2\text{O}(s) + \text{Ni}(s) \to \text{H}_2\text{O}(s)$</td>
<td>$1.000 \cdot 10^{-11}$</td>
<td>0.0</td>
</tr>
<tr>
<td>5. $\text{CO}_2 + \text{Ni}(s) \to \text{CO}_2(s)$</td>
<td>$1.000 \cdot 10^{-51}$</td>
<td>0.0</td>
</tr>
<tr>
<td><strong>Desorption:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6. $\text{CO} + \text{Ni}(s) \to \text{CO}(s)$</td>
<td>$5.000 \cdot 10^{-14}$</td>
<td>0.0</td>
</tr>
<tr>
<td>7. $\text{H}(s) + \text{H}(s) \to \text{Ni}(s) + \text{Ni}(s) + \text{H}_2$</td>
<td>$3.000 \cdot 10^{21}$</td>
<td>98.0</td>
</tr>
<tr>
<td>8. $\text{O}(s) + \text{O}(s) \to \text{Ni}(s) + \text{Ni}(s) + \text{O}_2$</td>
<td>$1.300 \cdot 10^{22}$</td>
<td>464.0</td>
</tr>
<tr>
<td>9. $\text{H}_2\text{O}(s) \to \text{H}_2\text{O} + \text{Ni}(s)$</td>
<td>$6.000 \cdot 10^{13}$</td>
<td>68.9</td>
</tr>
<tr>
<td>10. $\text{CO}(s) \to \text{CO} + \text{Ni}(s)$</td>
<td>$1.000 \cdot 10^{13}$</td>
<td>122.4</td>
</tr>
<tr>
<td>11. $\text{CO}_2(s) \to \text{CO}_2 + \text{Ni}(s)$</td>
<td>$1.000 \cdot 10^{8}$</td>
<td>27.3</td>
</tr>
<tr>
<td>12. $\text{CH}_4(s) \to \text{CH}_4 + \text{Ni}(s)$</td>
<td>$2.000 \cdot 10^{14}$</td>
<td>25.1</td>
</tr>
<tr>
<td>13. $\text{H}(s) + \text{O}(s) \to \text{OH}(s) + \text{Ni}(s)$</td>
<td>$5.000 \cdot 10^{22}$</td>
<td>97.9</td>
</tr>
<tr>
<td><strong>Surface reaction:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14. $\text{OH}(s) + \text{Ni}(s) \to \text{H}(s) + \text{O}(s)$</td>
<td>$3.000 \cdot 10^{20}$</td>
<td>34.3</td>
</tr>
<tr>
<td>15. $\text{H}(s) + \text{OH}(s) \to \text{H}_2\text{O}(s) + \text{Ni}(s)$</td>
<td>$3.000 \cdot 10^{20}$</td>
<td>42.7</td>
</tr>
<tr>
<td>16. $\text{H}_2\text{O}(s) + \text{Ni}(s) \to \text{H}(s) + \text{OH}(s)$</td>
<td>$3.000 \cdot 10^{22}$</td>
<td>87.0</td>
</tr>
<tr>
<td>17. $\text{OH}(s) + \text{OH}(s) \to \text{H}_2\text{O}(s) + \text{O}(s)$</td>
<td>$3.000 \cdot 10^{21}$</td>
<td>100.0</td>
</tr>
<tr>
<td>18. $\text{H}_2\text{O}(s) + \text{O}(s) \to \text{OH}(s) + \text{OH}(s)$</td>
<td>$3.000 \cdot 10^{21}$</td>
<td>207.5</td>
</tr>
<tr>
<td>19. $\text{C}(s) + \text{O}(s) \to \text{CO}(s) + \text{Ni}(s)$</td>
<td>$5.200 \cdot 10^{23}$</td>
<td>148.1</td>
</tr>
<tr>
<td>20. $\text{CO}(s) + \text{Ni}(s) \to \text{C}(s) + \text{O}(s)$</td>
<td>$2.500 \cdot 10^{21}$</td>
<td>139.7</td>
</tr>
<tr>
<td>21. $\text{CO}(s) + \text{O}(s) \to \text{CO}_2(s) + \text{Ni}(s)$</td>
<td>$2.000 \cdot 10^{20}$</td>
<td>123.6</td>
</tr>
</tbody>
</table>

The rate constant $A^*$ is given in units of molecules cm$^3$ mol$^{-1}$ s$^{-1}$, and $E^*$ is in kJ/mol. The units for the rate constants are $A^* = \text{cm}^3\text{mol}^{-1}\text{s}^{-1}$ and $E^* = \text{kJmol}^{-1}$.

Collaboration with Olaf Deutschmann, University of Karlsruhe

Authors: DECO MURI Colorado School of Mines University of Maryland California Institute of Technology
The separated-anode experiment is designed to isolate thermal heterogeneous chemistry.
Dry reforming (CO₂) is nearly as effective as steam reforming
Our models incorporate coupled fluid flow, thermal chemistry, and electrochemistry

<table>
<thead>
<tr>
<th>Approach</th>
<th>Reactive flow</th>
<th>Porous-media transport</th>
<th>Homogeneous chemistry</th>
<th>Heterogeneous chemistry</th>
<th>Electrochemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Performance</td>
<td>Efficiency</td>
<td>Utilization</td>
<td>Power density</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Design</td>
<td>MEA architecture</td>
<td>Catalyst materials</td>
<td>Electrode microstructure</td>
<td>Cell voltage</td>
<td>Flow rates</td>
</tr>
</tbody>
</table>

![Diagram of a fuel cell](image)
The models predict composition along the channels and through the electrodes.

Anode Inlet: 66% H₂, 22% CO, 12% CH₄, 30 cm/s, 800°C, 1 atm.
Cathode: Air
Efficiency, utilization, and power density depend greatly on operating voltage

- **Efficiency** and **Utilization**
- **Power density**

Conditions:
- $T = 800^\circ\text{C}$
- $U_{\text{in}} = 10 \text{ cm/s}$
- 50% CH$_4$
- 50% Air
- 1 mm$^2$ channel
Although understanding is advancing rapidly, much remains to be done

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### Charge-transfer chemistry
- Currently in modified BV form ==> Need elementary mechanisms
- Currently consider H2 ==> Need general mixed potential
- Limited validation data ==> Need validation data and theory

### Reforming and CPOX chemistry
- Current models for methane ==> Need higher hydrocarbons
- Current models for Ni ==> Consider alternative catalysts
- Assume inert ceramic supports ==> Investigate ceramic activity

### Cell and electrode optimization
- Structure drives performance ==> Functionally grade electrodes
- Alternative catalyst function ==> Functionally grade electrodes

### Coupling at the stack and system level
- Models are for single channel ==> Extend to full cell and stack
- Couple to thermal analysis ==> Depends on system boundaries
- Models for channels ==> Consider tube or sheet layout