Multi-scale modelling of backspillover process in CO Electrochemically Promoted oxidation for robust design and control of EPOC systems

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Motivation

The main motivation of this study is the formulation of accurate models and incorporation in the design of industrially used systems such as:

- Exhaust systems
- Solid Oxide Fuel Cell technology

Electrochemical Promotion of Catalysis

EPOC is the enhancement of catalytic activity by applying potential between a catalyst and a reference electrode due to an electrochemically controlled ion backspillover (migration) of species produced in the three phase boundaries (TPBs) (e.g. [O<sup>+</sup>· δ<sup>+</sup>]) forming a double layer which affects the binding strength of the adsorbed species [1].

EPOC leads to up to 1500% increase in the catalytic surface reaction rate [2].

- This enhancement is non-Faradaic and sometimes permanent under current interruption
- is also known as Non-Faradaic Electrochemical Modification of Catalytic Activity (NEMCA)

Objective

The formulation of an accurate model for an EPOC system so as to be used in conjunction with experimental data in order to:

- obtain insights on relevant complex phenomena
- compute reliable estimates for diffusion coefficients and rate constants
- ultimately enable EPOC system design

Effective Double Layer

Experimental Reactor

- Nano-patterned electrode in a well-mixed reactor
- Electrochemically Promoted oxidation of CO over Pt
- Large TPB length, low catalytic surface
- EPOC significant

Modelling Chemical Process [3]

Reactions

- \( O_2 (g) + 2 \cdot S \xrightarrow{k_1} 2O \cdot S \)
- \( CO (g) + \frac{k_1}{k_2} \xrightarrow{} CO \cdot S \)
- \( O \cdot S + CO \cdot S \xrightarrow{k_1} CO_2 \cdot S \xrightarrow{2 \cdot S} \)
- \( \left[ O^{2+} - \delta^+ \right] \cdot S + CO \cdot S \xrightarrow{k_1} CO_2 \cdot S \xrightarrow{2 \cdot S} \)
- \( 2\left[ O^{2+} - \delta^+ \right] \cdot S \xrightarrow{k_1} O_2 \cdot S \xrightarrow{2 \cdot S} \)

Reaction Rates

- \( r_1 = 2k_1C_0^\Theta^2 \)
- \( r_2 = k_2C_0^\Theta^2 \)
- \( r_3 = k_3\Theta_0\Theta_{CO} \)
- \( r_4 = k_4\Theta_{CO}\Theta_{RSS} \)
- \( r_5 = k_5\Theta_{RSS}^2 \)

Overall Species' Rates

- \( R_o = r_1 - r_3 \)
- \( R_{CO} = r_2 - r_5 \)
- \( K_{RSS} = r_4 - r_5 \)

Reaction Rate Constants

- \( k_i = k_{i0} \exp \left( \frac{-\Delta E_i - \Omega \Theta}{RT} \right), \quad i = 1,2,3 \)
- \( k_i = k_{i0} \exp \left( \frac{-\Delta E_i}{RT} \right), \quad i = 1,2 \quad k_i = k_{i0} = 10^2 s^{-1} \)

Concentration of species in gas

- \( C_i = \frac{P_i}{RT}, \quad i = O_2, CO \)

Conservation of surface sites

- \( \Theta_s = 1 - \Theta_0 - \Theta_{CO} - \Theta_{RSS} \)
Modelling Electrochemical Process [3]

**Electrochemical Reactions**

**Cathodic TPB**

\[
3 \times \left[ \frac{1}{2} O_{2 (e)} + 2e^- \rightleftharpoons O_{2 (a)} \]

**Cathodic Current Density**

\[
J^c = J^c_0 \left[ \exp \left( \frac{\alpha^c F \eta^c}{RT} \right) - \exp \left( -\alpha^c F \eta^c \right) \right]
\]

\[
J^c_0 = \frac{1}{3} \gamma V C_{O_2} \left( \frac{p_{O_2}}{p_{O_2}^0} \right)^{0.5} \exp \left( \frac{F \eta^c}{RT} \right)
\]

**Gas Phase**

\[
\eta^c = \eta^c_a + \eta^c_m = V_{O_2} \left( \Phi^c_a - \Phi^c_m \right)
\]

**Open Circuit Potential**

\[
V_{OC} = \frac{1}{3} \left( V_{O_2} \right) \left( \frac{p_{O_2}}{p_{O_2}^0} \right)^{0.5} \exp \left( \frac{F \eta^c}{RT} \right)
\]

**Anodic TPB**

\[
O_{2 (a)} \rightarrow CO_{2 (a)} + 2e^- + \frac{1}{2} \text{O}_2 \quad (i = 1, 2, 3)
\]

**Anodic Current Density**

\[
J^a = J_{i1}^a + J_{i2}^a + J_{i3}^a
\]

\[
J_{i1}^a = J_{i1}^{\alpha} \left[ \exp \left( \frac{\alpha^a F \eta^a_i}{RT} \right) - \exp \left( -\alpha^a F \eta^a_i \right) \right]
\]

**Boundary Conditions**

- Electrode (YSZ)
- Anode (Pt)

**Charge Conservation Equations**

**Microscopic Model Algorithm**

**Multi-scale Model Algorithm**

**3D Computational Domain**

- Dimensions vary from 50-200 nm

**Governing Equations and Boundary Conditions**

**Mass Conservation Equations (B1)**

\[
\frac{dP}{dt} + \nabla \cdot (\rho \nabla P) = -E_i \quad (i = 0, CO, BSS)
\]

**Boundary Conditions**

**Catalytic Monte Carlo (kMC) [4]**

- kMC for reaction-diffusion dynamics on catalytic surface B1 (Pt)

**Transition Probabilities**

\[
\Gamma = \Gamma_{d} + \Gamma_{pd} + \Gamma_{pjd} + \Gamma_{pjd}
\]

\[
\Gamma_{d} = k_d \cdot \rho \cdot \rho \cdot \rho \cdot \rho \cdot \rho \cdot \rho
\]

\[
\Gamma_{pd} = k_{pd} \cdot \rho \cdot \rho \cdot \rho \cdot \rho \cdot \rho \cdot \rho
\]

\[
\Gamma_{pjd} = k_{pjd} \cdot \rho \cdot \rho \cdot \rho \cdot \rho \cdot \rho \cdot \rho
\]

**Conditional Probabilities**

\[
\sum_{j} \left( \frac{\alpha_{i,j}}{1} \right) = 4 \Omega_i
\]

\[
\Omega_i = \sum_{j} \left( \frac{\alpha_{i,j}}{1} \right)
\]

\[
\Delta t = \log(1/R_i) / (\Omega_i \Gamma_{act})
\]

**Catalytic Micro-surface**

- 1200x200 sites micro-lattice

**Gap-Tooth**
Conclusions

- Development of a 3D Multi-scale model
  - 3D Macroscopic for charge balances
  - All the phenomena on the catalyst are modelled using kMC
  - 2D computational domain
  - Macro- and micro- are linked through fluxes
  - to from micro-surface
- Macro- and Multi- models
  - seem to exhibit similar dynamic trends
  - Quantitatively small discrepancies are observed

Future Work

- Enhancement of the model
  - to include heat balances (Joule heating)
- Parameter estimation
  - using experimental data currently underway
- To provide a quantitative understanding
  - of the complex phenomena taking place
  - EPOC system robust design and control
  - to enable this technology for industrial uses

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References

2. C.G. Vayenas, S. Bebela, C. Pliangos, S. Brosda, D. Tsiplakides, 2001;