



An electrochemical model for syngas production by co-electrolysis of H₂O and CO₂

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ABSTRACT

Co-electrolysis of CO₂ and H₂O in a solid oxide electrolyzer cell (SOEC) offers a promising way for syngas production. In this study, an electrochemical model is developed to simulate the performance of an SOEC used for CO₂/H₂O co-electrolysis, considering the reversible water gas shift reaction (WGS) in the cathode. The dusty gas model (DGM) is used to characterize the multi-component mass transport in the electrodes. The modeling results are compared with experimental data from the literature and good agreement is observed. Parametric simulations are performed to analyze the distributions of WGS and gas composition in the electrode. A new method is proposed to quantify the contribution of WGS to CO production by comparing the CO fluxes at the cathode–electrolyte interface and at the cathode surface. It is found that the reversible WGS could contribute to CO production at a low operating potential but consume CO at a high operating potential at an operating temperature of 1073 K and inlet gas composition (molar fraction) of H₂O: 49.7%, CO₂: 25%, H₂: 25%, CO: 0.3%. In addition, the contribution of WGS to CO production also depends on the operating temperature and inlet gas composition.

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1. Introduction

Hydrogen can be produced in a sustainable manner, such as by photocatalytic water splitting [1], gasification of biomass [2], solar thermochemical water-splitting [3], or water electrolysis driven by solar cells or wind turbines [4]. Among all the above technologies, water electrolysis is a practical and efficient method for large-scale hydrogen production. Alkaline electrolyzers and proton exchange membrane (PEM) electrolyzers usually work at room temperature. Solid oxide electrolyzer cells (SOECs) use the same materials with solid oxide fuel cells (SOFCs) but work in a reversed mode at a high temperature (i.e. 1073 K). Compared with alkaline and PEM electrolyzers, SOECs consume less electricity as part of the energy needed for water splitting is in the form of heat [5]. Because of their great potential, SOECs have received increasing interest in recent years [6–20]. Various materials have been developed to fabricate SOEC for hydrogen production by steam electrolysis [21–23]. Several mathematical models have been developed to predict the SOEC performance at various levels [24–32].

In addition to steam electrolysis, SOECs can be used to electrolyze CO₂ for CO and O₂ production [33–39]. Co-electrolysis of CO₂ and H₂O has also been demonstrated to be feasible for simultaneous production of H₂ and CO [33–44], which can be

subsequently processed for synthetic fuel production. In an SOEC used for H₂O/CO₂ co-electrolysis, 3 reactions take place simultaneously, namely H₂O electrolysis, CO₂ electrolysis, and reversible water gas shift reaction (WGS). A common understanding on co-electrolysis is that the reversible WGS should always contribute to CO production [38,40]. However, it is still not clear to which degree the reversible WGS is responsible for CO production in the SOEC [45]. In addition, the existing studies on H₂O/CO₂ co-electrolysis are all experimental in nature, with aims to demonstrate the feasibility of this technology or to develop new materials for performance improvement. The present literature is lacking detailed mathematical modeling of the SOEC used for H₂O/CO₂ co-electrolysis.

In this study, an isothermal electrochemical model is developed to characterize the performance of an SOEC used for CO₂/H₂O co-electrolysis. It is an extension of the previous models for CO₂ electrolysis and H₂O electrolysis, respectively [29,46]. Both the co-electrolysis and the reversible WGS inside the SOEC cathode are considered. The model is validated by comparing the simulation results with data from the literature. A new method is proposed to quantify the contribution of the reversible WGS to CO production by comparing the fluxes of CO at the cathode–electrolyte interface and at the cathode surface. The results show that the reversible WGS can produce or consume CO, depending on the average rate of WGS in the cathode. This is different from the common understanding on H₂O/CO₂ co-electrolysis. The electrochemical model will be extended to 2D/3D model in a subsequent study.

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2. Model development

2.1. Working principles

The working mechanisms of an SOEC for co-electrolysis of H₂O and CO₂ are shown in Fig. 1. In the SOEC, the gas mixture of H₂O, CO₂, H₂, and CO flows in the cathode channel while air flows in the anode channel. In the porous cathode, both H₂O and CO₂ molecules diffuse through the porous electrode to the triple-phase-boundary (TPB) at the cathode–electrolyte interface, where they are reduced to H₂ and CO via reactions (1) and (2), respectively.



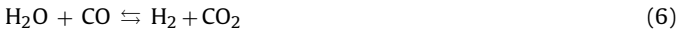
The oxygen ions (O²⁻) transport through the dense electrolyte to TPB at the electrolyte–anode interface, where they lose electrons to form oxygen molecules (Eq. (3)). The produced oxygen molecules subsequently diffuse through the porous anode to the anode surface and get collected.



The overall reactions for H₂O electrolysis and CO₂ electrolysis can be written as:



In addition to the above mentioned electrochemical reactions, reversible WGSR also occur in the cathode (Eq. (6)).



In operation, the required potential (*V*) applied to SOEC can be expressed as:

$$V = E + \eta_{act,a} + \eta_{act,c} + \eta_{ohmic} \quad (7)$$

where *E* is the equilibrium potential (Nernst potential); η_{ohmic} is the ohmic overpotential; $\eta_{act,a}$ and $\eta_{act,c}$ are the activation overpotentials at the anode and cathode, respectively.

2.2. Equilibrium potentials including concentration overpotentials

The concentration overpotentials are not explicitly expressed in Eq. (7) as they are implicitly included in the Nernst potentials (Eqs. (8) and (9)) for reactions (4) and (5), respectively [29,46]:

$$E_{\text{H}_2} = E_{\text{H}_2}^0 + \frac{RT}{2F} \ln \left[\frac{P_{\text{H}_2}^l \cdot (P_{\text{O}_2}^l)^{1/2}}{P_{\text{H}_2\text{O}}^l} \right] \quad (8)$$

$$E_{\text{CO}} = E_{\text{CO}}^0 + \frac{RT}{2F} \ln \left[\frac{P_{\text{CO}}^l \cdot (P_{\text{O}_2}^l)^{1/2}}{P_{\text{CO}_2}^l} \right] \quad (9)$$

where *E*⁰ is the voltage under standard conditions; $P_{\text{H}_2}^l$, $P_{\text{H}_2\text{O}}^l$, $P_{\text{CO}_2}^l$, P_{CO}^l and $P_{\text{O}_2}^l$ are the partial pressures of H₂, H₂O, CO₂, CO and O₂ at the electrolyte–electrode interface, respectively. *T* is temperature (K). *R* is the universal gas constant (8.3145 J mol⁻¹ K⁻¹); and *F* is the Faraday constant (96,485 C mol⁻¹). The *E*⁰ can be calculated from thermodynamics ($\Delta G/(2F)$). At 600 K and 1200 K, the values of *E*_{H₂}⁰ are 1.109017 V and 0.940172 V, respectively [47]. Similarly, the values of *E*_{CO}⁰ are 1.195502 V and 0.923869 V, respectively. Assuming linear variation of *E*⁰ between 600 K and 1200 K, the Nernst

potentials (including concentration overpotentials) for Eqs. (4) and (5) can be written as:

$$E_{E_2} = 1.253 - 0.00024516 T + \frac{RT}{2F} \ln \left[\frac{P_{\text{H}_2}^l (P_{\text{O}_2}^l)^{0.5}}{P_{\text{H}_2\text{O}}^l} \right] \quad (10)$$

$$E_{\text{CO}} = 1.46713 - 0.00045277 T + \frac{RT}{2F} \ln \left[\frac{P_{\text{CO}}^l (P_{\text{O}_2}^l)^{0.5}}{P_{\text{CO}_2}^l} \right] \quad (11)$$

2.3. Multi-component mass transfer in porous electrodes

In order to determine the gas partial pressures at the electrolyte–electrode interface, the multi-component reactive-transport processes in the porous electrodes must be solved (Eq. (12)). For modeling of multi-component reactive-transport in porous media, Fick's Model (FM), Stefan–Maxwell Model (SMM), and the Dusty-Gas Model (DGM) have been widely used in the literature [48]. The DGM is used in the present study due to its better accuracy for multi-component gas transport [49]. As the reversible WGSR does not change the total molar number of gas species, the pressure effect on mass transfer can be safely neglected [48,50]. According to DGM, the reactive-transport of gas species *i* can be expressed as [49]:

$$\frac{\varepsilon}{RT} \frac{\partial(y_i P)}{\partial t} = -\nabla N_i + R_i \quad (12)$$

$$\frac{N_i}{D_{i,k}^{eff}} + \sum_{j=1, j \neq i}^n \frac{y_j N_j - y_i N_j}{D_{ij}^{eff}} = -\frac{P}{RT} \frac{dy_i}{dx} \quad (13)$$

where *y_i* is the molar fraction of species *i*; ε is electrode porosity, *R_i* is the reaction rate (mol m⁻³ s⁻¹); $D_{i,k}^{eff}$ is the effective Knudsen diffusion coefficient (m² s⁻¹) of species *i*; D_{ij}^{eff} is the effective binary diffusion coefficient (m² s⁻¹) of species *i* and *j*; *P* is the pressure (Pa). *N_i* is the flux of species *i* (mol m⁻² s⁻¹). *d_c* and *d_a* are thicknesses of cathode and anode, respectively. *x* is the depth inside the electrode, measured from the electrode surface, as can be seen from the computational domain shown in Fig. 1.

The effective binary diffusion coefficient (D_{ij}^{eff}) can be evaluated as:

$$D_{ij}^{eff} = \frac{\varepsilon}{\xi} \frac{0.0026T^{1.5}}{p \sqrt{M_{i,j} \sigma_{i,j}^2 \Omega_D}} \quad (14)$$

$$M_{ij} = \frac{2}{(1/M_i) + (1/M_j)} \quad (15)$$

where ε/ξ is the ratio of porosity to tortuosity of porous electrodes; σ_{ij} is the mean characteristic length of species *i* and *j*; Ω_D is a dimensionless diffusion collision integral, which can be calculated as:

$$\sigma_{i,j} = \frac{\sigma_i + \sigma_j}{2} \quad (16)$$

$$\Omega_D = \frac{1.06036}{\tau^{0.1561}} + \frac{0.193}{\exp(0.47635\tau)} + \frac{1.03587}{\exp(1.52996\tau)} + \frac{1.76474}{3.89411\tau} \quad (17)$$

$$\tau = \frac{k_b T}{\varepsilon_{i,j}} \quad (18)$$

Here $k_b = 1.38066 \times 10^{-23}$ (J K⁻¹) is Boltzmann's constant. The values of σ_i and $\varepsilon_{i,j}$ can be used in the present study are summarized in Table 1 [51].

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