



Modeling of solid oxide electrolysis cell for syngas generation with detailed surface chemistry

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ARTICLE INFO

Article history:

Received 17 February 2012

Received in revised form 3 July 2012

Accepted 22 July 2012

Available online 10 August 2012

Keywords:

Elementary reaction

Electrolysis

Modeling

SOEC

ABSTRACT

A solid oxide electrolysis cell model for syngas generation is developed using a button cell test system as a physical base. The model coherently bridges the multi transport processes of charge, mass, momentum, and energy with detailed surface chemistry. The model is validated using experimental polarization curves. Upon the validation, extensive simulations are performed to elucidate surface electrolysis processes. Results indicate that the electrolysis processes of CO₂ and H₂O are pretty much independent with each other in the H₂ electrode (electrolysis cathode). The carbon coking effect is mainly determined by the content of CO₂ in the H₂ electrode. Increasing the applied cell voltage may improve syngas production, it also causes the enhancement of the surface coverage of C(s) and the deposition of carbon on the surface of Ni catalyst. High operating temperature may effectively improve adsorption/desorption rate and enhance surface electrolysis process as well as potentially mitigate carbon deposition on Ni surface.

Published by Elsevier B.V.

1. Introduction

The potential fossil fuel crisis and climate changes raise the need to develop renewable and clean energy technology [1]. The co-electrolysis of H₂O and CO₂ using the inverse process of solid oxide fuel cell (SOFC) is able to produce synthetic gas in a clean and efficient way [2,3]. Such a technique has been demonstrated experimentally and attracted much interest recently [4]. Since experimental technique is limited in probing complicated transport and surface chemistry particularly in porous electrodes, modeling method as a complementary technique has been resorted extensively.

There have been recent studies on numerical modeling of solid oxide electrolysis cell (SOEC), including H₂O electrolysis [5–8] and CO₂ electrolysis [9–11]. Usually such models are a global type of kinetic models, where the concentrations of bulk gas species are used for Butler–Volmer equation to couple electrochemical reactions with transport process in porous electrodes. As a consequence, the adsorbed species on electrode surface and surface reactions are neglected. To overcome this issue, the elementary kinetic modeling approach is recently investigated [12–18] to describe the adsorption/desorption processes and the detailed surface chemistry via individual reaction steps. While elementary kinetic model is able to provide more precise electrochemical charge-transfer calculation, such a model is limited to describe the reaction process at one individual point on the electrode surface. Currently there is a lack of coherent integration between macro-scale transport processes and local elementary kinetic reactions. On the other hand,

the elementary kinetic models are mainly studied for SOFCs [13–18], there is little efforts for SOEC modeling [12].

In this paper, a SOEC model for the simulation of synthetic gas generation is developed, bridging macro-scale transport processes with elementary kinetic reactions in a coherent way. A button cell test system is used as a physical base for modeling demonstration.

2. Mathematical model

Shown in Fig. 1 is a typical button cell test stand. An anode-supported button cell is fixed at the top of a vertical large ceramic tube. A small vertical ceramic tube is used to supply steam (H₂O) and CO₂ to the H₂ electrode. The temperature of this test stand is controlled by a test furnace. When an external voltage greater than the open circuit voltage of the cell is applied to the cell, electrolysis process takes place. Overall, O₂ is generated at the anode side (O₂ electrode) while H₂ and CO are produced at the cathode side (H₂ electrode). In the following, the detailed reaction steps will be studied.

2.1. Heterogeneous surface chemistry in electrodes

In principle, the heterogeneous chemical/electrochemical processes take place on the SOEC electrode surface, which are affected by not only the applied catalysts and materials but also the porous structure of electrodes. For H₂-electrode supported Ni–YSZ/YSZ/LSM button cell, the surface chemical processes are usually more complicated on H₂ electrode side than those on O₂ electrode side due to both the active catalytic function of Ni and the complicated fuel/gas compositions. Table 1 provides twenty one reversible elementary reactions

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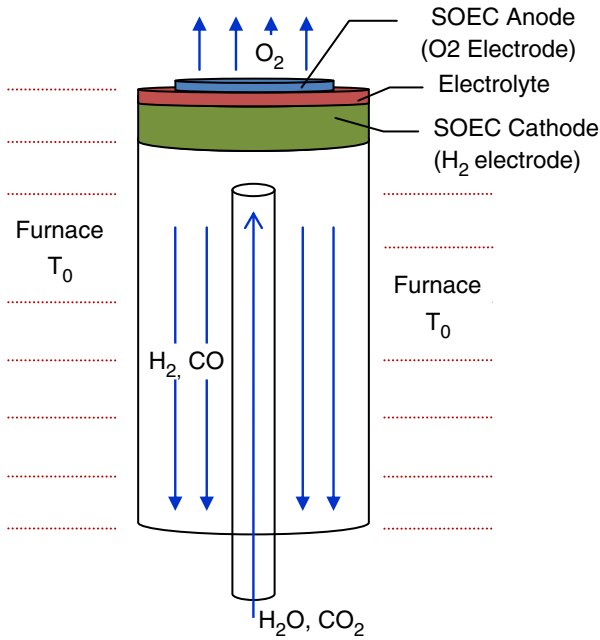


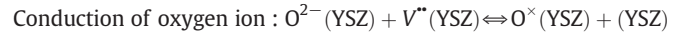
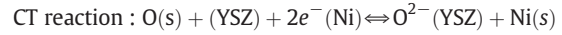
Fig. 1. Schematic of the gas flow and SOEC operation.

of syngas fuel on Ni surface proved by experiments, where two types of processes can be identified: the adsorption/desorption process and surface reaction process. Basically, the adsorption/desorption process is the first step for syngas species to be adsorbed on the electrode surface, then the surface reactions take place among all adsorbates and reaction intermediates. According to molecular behavior, none of the electrochemical reaction and charge transfer process takes place on the catalytic Ni surface, but on Ni-YSZ surface (triple phase boundary), several charge transfer pathways could exist simultaneously [13]. Since the kinetics of charge transfer (CT) steps are not

Table 2
Reaction rates and source terms.

Net reaction rate of adsorbates	Reaction source term	Energy source term
$r_{CH4(s)} = r_3 - r_{14} - r_{18}$	$R_{H_2} = -2r_1$	$R_{Ca} = Q_{ohm} + Q_{elec/chem}$
$r_{CH3(s)} = r_{14} - r_{15} + r_{18} - r_{19}$	$R_{CH_4} = -r_2$	$R_{EI} = Q_{ohm}$
$r_{CH2(s)} = r_{15} - r_{16} + r_{19} - r_{20}$	$R_{H_2O} = -r_4$	$R_{An} = Q_{ohm} + Q_{elec/chem}$
$r_{CH(s)} = r_{16} - r_{17} + r_{20} - r_{21}$	$R_{CO_2} = -r_5$	$R_{CI} = 0$
$r_{C(s)} = -r_{10} + r_{17} + r_{21}$	$R_{CO} = -r_6$	
$r_{CO(s)} = r_6 + r_{10} - r_{11} + r_{12}$		
$r_{CO2(s)} = r_5 + r_{11}$		
$r_{H(s)} = 2r_1 - r_7 - r_8 + r_{12} + r_{14} + r_{15} + r_{16} + r_{17}$		
$r_{OH(s)} = r_7 - r_8 - r_9 + r_{13} + r_{18} + r_{19} + r_{20} + r_{21}$		

directly available from experiments, Bessler et al. [13,15,16] have proposed several possible types of CT reactions and taken them as free fit parameters to compare model predictions with experimental results. It was found that all proposed CT mechanisms can fit the experiment results well except the double oxygen-spillover CT mechanisms which would fail to give correct predictions when the electrode was polarized under high steam partial pressures. Thus, in our modeling, a single-step reversible CT mechanism is assumed at the triple phase boundary, i.e., the adsorbed oxygen ions gain/release all electrons on the Ni-YSZ surface by one step reaction, and is expressed as,



here, $O^{\times}(YSZ)$ is the lattice oxygen, $V^{**}(YSZ)$ is the oxygen vacancy, $O(s)$ is the adsorbed oxygen ion on Ni surface. The elementary kinetic reaction rate can be formulated by,

$$i_{F,an} = nF I_{tpb} (k_f \theta_{O^{2-}(YSZ)} \theta_{Ni} - k_b \theta_{O(s)}) \quad (1)$$

Table 1
Surface reaction mechanism.

Ni-surface [17,20]	A	n	E
<i>Adsorption/desorption (f;b)</i>			
1 $H_2 + Ni(s) + Ni(s) \rightleftharpoons H(s) + H(s)$	10^{-2} ; 5.593×10^{19}	0 ; 0	0 ; 88.12
2 $O_2 + Ni(s) + Ni(s) \rightleftharpoons O(s) + O(s)$	10^{-2} ; 2.508×10^{23}	0 ; 0	0 ; 470.39
3 $CH_4 + Ni(s) \rightleftharpoons CH_4(s)$	8×10^{-3} ; 5.302×10^{15}	0 ; 0	0 ; 33.15
4 $H_2O + Ni(s) \rightleftharpoons H_2O(s)$	1×10^{-1} ; 4.579×10^{12}	0 ; 0	0 ; 62.68
5 $CO_2 + Ni(s) \rightleftharpoons CO_2(s)$	1×10^{-5} ; 9.334×10^7	0 ; 0	0 ; 28.80
6 $CO + Ni(s) \rightleftharpoons CO(s)$	5×10^{-1} ; 4.041×10^{11}	0 ; 0	0 ; 112.85
<i>Surface reactions</i>			
7 $O(s) + H(s) \rightleftharpoons OH(s) + Ni(s)$	5×10^{22} ; 2.005×10^{21}	0 ; 0	97.9 ; 37.19
8 $OH(s) + H(s) \rightleftharpoons H_2O(s) + Ni(s)$	3×10^{20} ; 2.175×10^{21}	0 ; 0	42.7 ; 91.36
9 $OH(s) + OH(s) \rightleftharpoons O(s) + H_2O(s)$	3×10^{21} ; 5.423×10^{23}	0 ; 0	100 ; 209.37
10 $O(s) + C(s) \rightleftharpoons CO(s) + Ni(s)$	5.2×10^{23} ; 1.418×10^{22}	0 ; -3	148.1 ; 115.97
11 $O(s) + CO(s) \rightleftharpoons CO_2(s) + Ni(s)$	2×10^{19} ; 3.214×10^{23}	0 ; -1	123.6 ; 86.5
12 $HCO(s) + Ni(s) \rightleftharpoons CO(s) + H(s)$	3.7×10^{21} ; 2.338×10^{20}	0 ; -1	0 ; 127.98
13 $HCO(s) + Ni(s) \rightleftharpoons O(s) + CH(s)$	3.7×10^{24} ; 7.914×10^{20}	-3 ; 0	95.8 ; 114.22
14 $CH_4(s) + Ni(s) \rightleftharpoons CH_3(s) + H(s)$	3.7×10^{21} ; 4.438×10^{21}	0 ; 0	57.7 ; 58.83
15 $CH_3(s) + Ni(s) \rightleftharpoons CH_2(s) + H(s)$	3.7×10^{24} ; 9.513×10^{22}	0 ; 0	100 ; 52.58
16 $CH_2(s) + Ni(s) \rightleftharpoons CH(s) + H(s)$	3.7×10^{24} ; 3.008×10^{24}	0 ; 0	97.1 ; 76.43
17 $CH(s) + Ni(s) \rightleftharpoons C(s) + H(s)$	3.7×10^{21} ; 4.4×10^{22}	0 ; 0	18.8 ; 160.49
18 $CH_4(s) + O(s) \rightleftharpoons CH_3(s) + OH(s)$	1.7×10^{24} ; 8.178×10^{22}	0 ; 0	88.3 ; 28.72
19 $CH_3(s) + O(s) \rightleftharpoons CH_2(s) + OH(s)$	3.7×10^{24} ; 3.815×10^{21}	0 ; 0	130.1 ; 21.97
20 $CH_2(s) + O(s) \rightleftharpoons CH(s) + OH(s)$	3.7×10^{24} ; 1.206×10^{23}	0 ; 0	126.8 ; 45.42
21 $CH(s) + O(s) \rightleftharpoons C(s) + OH(s)$	3.7×10^{21} ; 1.764×10^{21}	0 ; 0	48.1 ; 129.08
<i>Ni/YSZ-surface (Charge transfer reactions) [13,15,16]</i>			
1 $O^{\times}(YSZ) + (YSZ) \rightleftharpoons O^{2-}(YSZ) + V^{**}(YSZ)$	A^0	α	E
2 $O^{2-}(YSZ) + Ni(s) \rightleftharpoons O(s) + (YSZ) + 2e^-(Ni)$	1.6×10^{22}	0	90.9
	4.9×10^{-6}	0.5	c

Rate constant of Arrhenius equation written as: $k = A \exp(-E/RT)$, the unit of Eis kJ/mol. c—Calculated or estimated from references.

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