Journal of Power Sources 379 (2018) 298–308

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Elementary reaction modeling of reversible CO/CO_2 electrochemical conversion on patterned nickel electrodes

Yu Luo[a], Yixiang Shi[a,*], Wenying Li[a,b], Ningsheng Cai[a]

[a] Key Laboratory for Thermal Science and Power Engineering of Ministry of Education, Department of Energy and Power Engineering, Tsinghua University, Beijing 100084, China
[b] Sichuan Energy Internet Research Institute, Tsinghua University, Sichuan 610213, China

HIGHLIGHTS

- Pattered electrode elementary reaction modeling.
- Proposing carbon-related charge transfer step.
- Contributions of reaction steps in SOFC/SOEC operation mode.

ARTICLE INFO

Keywords:
Reversible solid oxide cell
Patterned electrode
Carbon monoxide
Carbon dioxide
Elementary reaction model
Carbon

ABSTRACT

CO/CO_2 are the major gas reactant/product in the fuel electrode of reversible solid oxide cells (RSOC). This study proposes a two-charge-transfer-step mechanism to describe the reaction and transfer processes of CO-CO_2 electrochemical conversion on a patterned Ni electrode of RSOC. An elementary reaction model is developed to couple two charge transfer reactions, $C(Ni) + O^{2-}(YSZ) \leftrightarrow CO(Ni) + (YSZ) + 2e^-$ and $CO(Ni) + O^{2-}(YSZ) \leftrightarrow CO_2(Ni) + (YSZ) + 2e^-$, with adsorption/desorption, surface chemical reactions and surface diffusion. This model well validates in both solid oxide electrolysis cell (SOEC) and solid oxide fuel cell (SOFC) modes by the experimental data from a patterned Ni electrode with 10 μm stripe width at different pCO (0–0.25 atm), pCO_2 (0–0.35 atm) and operating temperature (600-700 °C). This model indicates SOEC mode is dominated by charge transfer step $C(Ni) + O^{2-}(YSZ) \leftrightarrow CO(Ni) + (YSZ) + 2e^-$, while SOFC mode by $CO(Ni) + O^{2-}(YSZ) \leftrightarrow CO_2(Ni) + (YSZ) + 2e^-$ on the patterned Ni electrode. The sensitivity analysis shows charge transfer step is the major rate-determining step for RSOC, besides, surface diffusion of CO and CO_2 as well as CO_2 adsorption also plays a significant role in the electrochemical reaction of SOEC while surface diffusion of CO and CO_2 desorption could be co-limiting in SOFC.

1. Introduction

Power-to-gas (PtG) enables to seasonally store intermittent renewable power in the form of chemical energy, particularly, mobile fuel gas makes it possible to transport stored renewable power in a wider area. PtG by reversible solid oxide cells (RSOC) can integrate power storage device and power generation device to offer a compact and efficient pathway for distributed renewable power systems. For power storage, RSOC can operate in solid oxide electrolysis cell (SOEC) mode to split H_2O/CO_2 into H_2/CO even other hydrocarbon fuels by means of electrical energy. Oppositely, RSOC can also operate in solid oxide fuel cell (SOFC) mode to stably generate electricity when fed with fuels. Conventionally, H_2-H_2O electrochemical conversion is widely studied in SOEC [1–3] and SOFC [4–7]. Oxygen-ion-conducting electrolyte makes direct electrochemical reduction of CO_2 and electrochemical oxidation of CO possible in RSOC, hence, carbon neutral and renewable power storage can be synchronously realized. A considerable part of studies focus on CO-CO_2 electrochemical conversion in SOFC [8–15] or SOEC [16–21]. Compared with H_2-H_2O electrochemical conversion, CO-CO_2 electrochemical conversion has different reaction and transfer processes in the fuel electrode of RSOC. Currently, the most common and practical fuel electrode is Ni-YSZ electrode with porous structure [3,8,16–18]. However, the complexity of porous structure introduces the difficulty in the estimation of effective reaction active sites as well as the interference of bulk diffusion. From the perspective of mechanism understanding, a regular and simply electrode structure is

---

[*] Corresponding author.
E-mail address: shyx@tsinghua.edu.cn (Y. Shi).

https://doi.org/10.1016/j.jpowsour.2018.01.016
Received 8 November 2017; Received in revised form 17 December 2017; Accepted 7 January 2018
0378-7753/

more applicable. Patterned Ni electrode is such a simplified electrode with two-dimension regular geometric pattern. In a patterned Ni electrode, the electrochemical reaction active sites (triple phase boundary, TPB) and chemical reaction active sites (Ni surface) can be accurately calculated, meanwhile, the interference of microstructure in gas transport is well excluded.

For CO-CO_2 electrochemical conversion, the main half reaction between CO and CO_2 in the fuel electrode is usually expressed as:

$$CO(g) + O^{2-}(YSZ) \underset{SOEC}{\overset{SOFC}{\rightleftarrows}} CO_2(g) + 2e^- \tag{1}$$

Present mechanism studies on fuel electrodes of RSOC in CO-CO_2 atmosphere aim at mainly CO electrochemical oxidation in SOFC mode [9,11–13,22–27], but few at CO_2 electrochemical reduction in SOEC mode [28–30]. A patterned Ni electrode was measured in SOFC mode by Utz et al. [11] to show positive dependencies of the electrochemical performance on $p\mathrm{CO_2}$ and T, as well as a varied dependency on pCO. The dependency of the electrochemical performance on pCO was found to be positive for $p\mathrm{CO} < 0.2$ atm and negative for a higher pCO. Boulenouar et al. [27] studied the electrochemical impedance spectroscopy (EIS) of CO electrochemical oxidation on a grid Ni electrode. EIS revealed only one relaxation times at low ratio of $p\mathrm{CO_2}/p\mathrm{CO}$ but multiple relaxation times at high $p\mathrm{CO_2}/p\mathrm{CO}$, which implied that CO, O and CO_2 could be related to CO electrochemical oxidation mechanism. Sukeshini et al. [22] concluded that surface diffusion of CO and CO adsorption on Ni surface could be non-ignorable in SOFC mode on the basis of the experiment on patterned Ni electrodes in CO-CO_2 atmosphere. An experiment on a porous Ni-YSZ electrode by Matsuzaki et al. [31] also showed CO surface diffusion is rate-limiting. But they believed that charge transfer step becomes co-limiting at a temperature of around 1000 °C.

For more insight into reaction mechanism, experiment should be combined with quantitative model analysis. Existing model studies widely use oxygen spillover mechanism to describe the charge transfer reaction in CO-CO_2 atmosphere [9,10,12,13,18,23,25]. Lauvstad et al. [25,26] built an analytical model to evaluate possible CO oxidation reaction mechanisms. They speculated that gaseous CO_2 is produced from the combination of adsorbed CO on Ni surface and adsorbed O on YSZ surface. Hanna et al. [9] built a simplified mechanism for the description of CO electrochemical oxidation on patterned Ni electrodes. This work proved that CO(Ni) surface diffusion from Ni surface to TPB is rate-limiting. Shi et al. [23] built a more detailed elementary reaction model according to the heterogeneous thermochemistry mechanism proposed by Hecht et al. [32] and Janardhanan et al. [33]. This model was able to predict EIS well at different temperature, and also implied that surface diffusion could be one of rate-determining steps at lower temperature and higher polarization voltage. Yurkiv et al. [12,13] summarized a set of complete thermodynamic data for gaseous, surface and bulk species, as well as kinetics parameters for the Ni/YSZ surface reactions, based on which an elementary reaction model was built to couple the Ni and YSZ surface reactions, 3 charge transfer reactions as well as surface diffusion. This model was respectively validated by Lauvstad et al.'s experiment [26] and Utz's experiment [11]. A mechanism was identified in which O^{2-}(YSZ) is converted via O^-(YSZ) to O(Ni). Besides, charge transfer step from O^-(YSZ) to O(YSZ) and surface diffusion of adsorbed O on YSZ surface were found to be also colimiting at low $p\mathrm{CO}/p\mathrm{CO_2}$.

Previous studies [34] from our group have measured the dependency of the electrochemical performance of patterned Ni electrode on pCO, $p\mathrm{CO_2}$ and T in both SOEC and SOFC modes. When it comes to the reversed process of SOFC, a similar elementary reaction mechanism was applied for porous Ni-YSZ electrode in SOEC mode [18]. Nevertheless, the experimental evidence was shown that the electrochemical performance in SOFC mode is 4–6 folds as high as that in SOEC mode [29]. The phenomenon implies that the rate-determining steps could be different between SOEC and SOFC modes. In addition, different phenomena on carbon deposition were also found in these two modes [28]. Crystal graphitic carbon is believed to be consumed at TPB in SOFC mode, while generated at TPB in SOEC mode. Therefore, CO electrochemical reduction process related to carbon deposition could be non-ignorable for CO-CO_2 electrochemical conversion, which was proposed by Li et al. [28] as below:

$$C(Ni) + O^{2-}(YSZ) \underset{SOEC}{\overset{SOFC}{\rightleftarrows}} CO(Ni) + (YSZ) + 2e^- \tag{2}$$

This step is considered to be significant at extremely high polarization voltage [35], and generally negligible in previous elementary reaction SOFC models [9,12,13,25]. However, a subsequent experiment on a patterned Ni electrode manifested that the electrochemical performance of the patterned Ni electrode fed with pure CO was 2–3 folds of that of the patterned Ni electrode fed with pure CO_2 in SOEC mode [34]. An analytical calculation also reveals CO electrochemical reduction could dominate in the SOEC mode [34].

In this paper, an elementary reaction model is built to couple adsorption/desorption, surface chemical reactions and surface diffusion. Two charge-transfer steps are considered in this model to enable to describe the elementary steps contained in both Eq. (1) and Eq. (2). The experiment on a patterned Ni electrode with 10 μm stripe width [34] is used for model validation in both SOEC and SOFC modes. The combination of mechanistic model and experiment can offer a quantitative interpretation for the experimentally observed phenomena.

2. Model development

2.1. Mechanism for heterogeneous chemical and electrochemical reactions

In this model, the heterogeneous reaction mechanism uses the mechanism in CO-CO_2 atmosphere simplified from the methane reforming elementary reaction mechanism summarized by Hecht et al. [32] and Janardhanan et al. [33]. For electrochemical reactions, two charge-transfer steps for oxygen spillover are considered: one is the reversible step to convert between adsorbed CO(Ni) and CO_2(Ni) [9,18,23,36], the other one is the reversible step to convert between adsorbed C(Ni) and CO(Ni) [28]. The heterogeneous chemical reactions and charge transfer reactions are summarized in Table 1. Here, some kinetic parameters expressed as a symbol should be particularly noticed. $\theta_{\mathrm{CO(Ni)}}$, the local CO(Ni) coverage, could vary with location, gas composition, temperature and so on, hence, should be coupled with other reactions and transfer equations. CO_2 adsorption is more likely to occur on the surface offering abundant oxygen in gas phase or lattice oxygen/defects on surface [29,37], hence, CO_2 could mainly adsorb near TPB or at TPB. A porous cermet Ni/YSZ electrodes has a disperse distribution of metal oxide surfaces and Ni-YSZ interfaces, where TPB density is $\sim 10^{12}\,\mathrm{m\,m^{-3}}$ [29,38]. However, TPB density of a patterned Ni electrode is three orders of magnitude less than that of porous cermet electrodes [29,38]. The active sites for CO_2 adsorption are greatly inhibited. Therefore, the kinetics of CO_2 adsorption ($\mathrm{R1_f}$) for patterned Ni electrodes is slower than that for porous cermet electrodes. The kinetic parameters proposed by Hecht et al. [32] and Janardhanan et al. [33] are applied for the metal oxide supported Ni-based catalysts, and should be modified for the application of patterned Ni electrode. Here, the pre-exponential factor for CO_2 adsorption ($\mathrm{R1_f}$) is a tuning parameter determined by experimental data. In addition, kinetic parameters for charge transfer steps are unknown and also tuned to fit the experimental data.

2.2. Model assumpon domains

The model is built according to a tested patterned Ni button cell with the stripe width of 10 μm, as shown in Fig. 1(a) [34]. The patterned Ni electrode is fuel electrode, dense single-crystal YSZ is electrolyte and porous Pt electrode is air electrode of this button cell. The