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Review

High temperature solid oxide H_2O/CO_2 co-electrolysis for syngas production

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ABSTRACT

High temperature H_2O/CO_2 co-electrolysis using solid oxide electrolysis cells is a promising method to produce syngas (a mixture of H_2 and CO), which can be used as feedstock of the Fischer-Tropsch reaction to synthesize value added liquid fuels. However, the overall solid oxide co-electrolysis process is complicated, involving both electrochemical reaction and reverse water gas shift reaction. The present paper offers a brief overview of the fundamental knowledge related to solid oxide co-electrolysis cells, such as working principle, thermodynamics and Nernst potentials. In addition, chemical equilibrium co-electrolysis models are reviewed, which have been developed to reveal the systematic relationship between the operating conditions and the Nernst potential as well as the gas composition evolution. Finally, the electrochemical performances recently reported on a number of solid oxide co-electrolysis cells are summarized, and cell degradation mechanisms occurred on solid oxide cells using Ni-based cermets cathode are also reviewed.

Contents

1. Introduction

In the past several decades, global industrialization has led to an ever-increasing demand for fossil fuels such as coal, petroleum and natural gas. The burning of carbon-based fossil fuels has released a significant amount of greenhouse gases, which greatly contribute to the global warming and intense weather phenomena [1–3]. Consequently, there is an urgent need to develop environmental friendly alternatives to fossil fuels and carbon-neutral energy technologies to solve the energy and environmental problems [1,4]. Hydrogen is probably one of the most ideal energy carriers as future fuel because of its clean combustion.

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However, the well-known difficulties in hydrogen storage that need extensive technological development as well as additional hydrogen infrastructure investment slow down the path of the hydrogen fuel applications [5–7]. As a result, synthetic liquid fuels are subsequently proposed as alternatives to hydrogen because of the better storability and transportability [8,9]. The similarity of synthetic liquid fuels to current hydrocarbon fossil fuels makes them able to use the existing infrastructure for storage and transportation without too much modification. Moreover, compared to hydrogen, liquid fuels exhibit higher energy density, indicating less fuel storage volume and thus less investment cost on capital [9]. Therefore, liquid fuels are promising energy carriers for future energy application.

Recently, investments on renewable and sustainable energy sources such as wind, solar, hydra and tidal have rapidly grown to produce primary electricity [10]. However, the intermittency nature of most renewable sources has resulted in tremendous challenges in grid management. Consequently, large scale energy conversion and storage are inevitable in a sustainable future energy system [5,11]. Solid oxide co-electrolysis cell offers a promising way to convert electrical energy to chemical energy by splitting steam and CO_2 into synthesis gas (syngas, a mixture of CO and H_2), which can later be used as feedstock for the synthetic fuel production via the Fischer-Tropsch (F-T) process [6,7]. Moreover, when the power supply is lower than the demand, solid oxide cells (SOCs) could also be operated reversely to convert the chemical energy back into electricity in the solid oxide fuel cell (SOFC) mode [7,9]. Therefore, SOCs can serve as novel energy conversion device to achieve a balance between fuel production and electricity generation. Noting that the amount of CO_2 consumed in the co-electrolysis process is the same as that produced in oxidizing the synthetic fuel, an overall CO_2 neutral cycle could be established by combining the solid oxide co-electrolysis cell with CO_2 capture technologies [12,13]. Therefore, it is necessary to develop solid oxide co-electrolysis cell for large-scale application of clean energies and the reduction of CO_2 emissions.

Steam and CO_2 could be split separately and then mixed together to form syngas. However, there are some significant advantages to split steam and CO_2 simultaneously via co-electrolysis process. First of all, it is more cost effective and energy efficient to conduct the co-electrolysis due to the fast overall electrochemical kinetics [7,14]. The electrochemical performance of co-electrolysis reaction is close to that of sole steam electrolysis, but dry CO_2 electrolysis has a much higher activation energy demand due to the slow CO_2 splitting kinetics. Consequently, co-electrolysis shows a relatively lower polarization resistance and overpotential in comparison to sole CO_2 electrolysis [6,14–16]. Second, a great amount of CO_2 conversion to CO in the co-electrolysis operation proceeds in a reverse water gas shift (RWGS) chemical reaction ($H_2(g) + CO_2(g) \rightarrow CO(g) + H_2O(g)$) which results in a remarkable reduction of the total electrical consumption to produce syngas [17]. Third, carbon deposition could be effectively suppressed by introducing steam into CO_2 during the co-electrolysis process, whereas in case of dry CO_2 electrolysis, CO_2 could be deeply split to carbon, causing severe coking and loss of cell function [18,19]. Therefore, high temperature steam/CO_2 co-electrolysis is a highly efficient technology for syngas production with lower cost and enhanced durability.

However, it should be noted that the co-electrolysis reaction which involves five gas species of CO_2, H_2, CO, H_2O and O_2 is much more complicated than sole steam or CO_2 electrolysis where the RWGS reaction occurs simultaneously with the electrolysis reaction, and each of which must be properly quantified to evaluate the overall syngas production results [6,20–23]. In addition, unlike the linear correlation between current density and H_2/CO production rate described in the Faraday's law for separate H_2O or CO_2 electrolysis, the electrochemical performance and product composition are directly related to the cell operating conditions including inlet gas composition, operating temperature and applied voltage or current [24–26]. For this reason, it is not adequate to use sole parameter of current density to evaluate the electrochemical performance and product composition. Therefore, to better understand and guide the syngas production via the solid oxide co-electrolysis cell, the correlation between the operating conditions and electrochemical performance should be systematically explored, and the conventional research means for separate H_2O and CO_2 electrolysis need to be modified accordingly. Recently, a great number of researches have been focused on the electrochemical performance of the solid oxide co-electrolysis cell, although much less research has concentrated on the outlet gas composition and reaction mechanism, which require a further and more systematic study.

In this paper, working principles and thermodynamics for the co-electrolysis process are presented to provide a general overview of the solid oxide co-electrolysis technology. Models to determine the Nernst potential and outlet gas composition are highlighted to reveal the systematic relationship between the operating conditions and performance of the electrochemical cell and syngas production. Materials for solid oxide co-electrolysis cell, electrochemical performance and degradation issues of solid oxide co-electrolysis cells are also summarized. The objective of this work is to provide a brief review on recent progresses for high temperature solid oxide co-electrolysis technology.

2. Description of solid oxide co-electrolysis process

2.1. Working principle

Fig. 1 shows the working principle of solid oxide co-electrolysis cell for syngas production. A gas stream composed of steam and CO_2 is supplied to the cathode, where the reactants receive electrons supplied from the external power to produce syngas (H_2 and CO) as well as the oxygen ions [7].

$$CO_2(g) + 2e^- \rightarrow CO(g) + O^{2-} \quad (1)$$

$$H_2O(g) + 2e^- \rightarrow H_2(g) + O^{2-} \quad (2)$$

The oxygen ions are then transported across the dense electrolyte from the cathode to the anode side under the driving force of applied voltage higher than the Nernst potential to overcome oxygen partial pressure gradient, and the arrived oxygen ions are subsequently oxidized to oxygen gas, releasing the electrons.

$$2O^{2-} \rightarrow O_2(g) + 4e^- \quad (3)$$

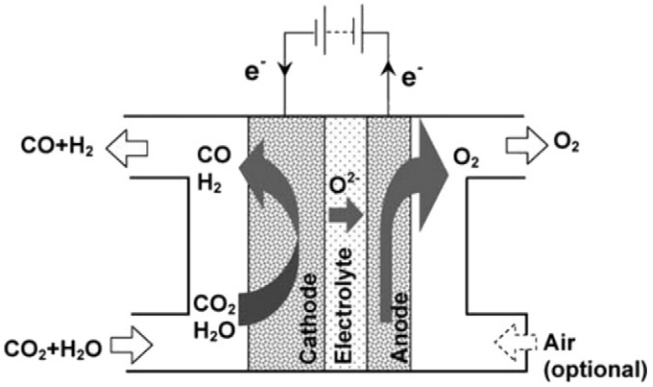

Fig. 1. Working principles of a solid oxide electrolysis cell (SOEC) for the co-electrolysis of steam/CO_2 process [7].
(Reproduced from Ref. [7] with permission from The Royal Society of Chemistry).