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Co-electrolysis for power-to-methanol applications

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ABSTRACT

This article reviews the issues facing co-electrolysis and its applications to the power-to-methanol process. Co-electrolysis is an attractive process for syngas production that uses excess generated electricity. In extended applications, syngas produced from co-electrolysis can be used for various applications like methanol production. In this review, the power-to-methanol process is comprehensively discussed from a process systems engineering viewpoint. The subjects discussed include the reason to choose methanol as a final product, the latest progress in power-to-methanol projects, and a comparison of methanol production from H_2-CO (from co-electrolysis) and H_2-CO_2 mixtures (from electrolysis). Syngas production pathways from co-electrolysis and electrolysis are further investigated, and potential power-to-methanol schemes using co-electrolysis are deployed. Lastly, research directions are proposed to accelerate power-to-methanol commercialization.

1. Introduction

Fossil fuel use causes environmental problems, such as pollution, global warming, and climate change. Several attempts to limit fossil fuel use and reduce their carbon footprints have emerged. The most renowned is the use of renewable energy sources. However, a notorious drawback of renewable energy is its intermittency. For example, in May 2016, the electricity supply in Germany far exceeded demand, the price of electricity became negative, and people were paid to consume electricity [1]. This condition is not favorable for independent renewable power producers and may hamper renewable energy development.

Currently, fossil fuels are still used in energy-intensive industries and power plants. Thus, carbon capture and utilization (CCU) has also been proposed as a solution to reduce the industrial carbon footprint. Power-to-methanol (PtM), sometimes called emission-to-methanol, is one of the CCU technology. PtM process depicted in Fig. 1 consists of three main steps in general: (1) the production of H_2 from (renewable) electricity using water electrolysis, (2) the utilization of CO_2, and (3) the synthesis and purification of methanol. In this way, the electric energy can be converted to and stored as methanol. This contributes not only to the stable operation of the renewable energy grid but also to utilizing CO_2 generated from industry or power plants.

An alternative technology to convert renewable electricity to syngas is co-electrolysis (sometimes called syntrolysis). In co-electrolysis, water and CO_2 are electrolyzed at the same time, while the reverse water-gas shift (RWGS) reaction is also occurring. The respective contribution of electrolysis and RWGS reaction to the conversion of CO_2 to CO was quantified by Ni [2]. Co-electrolysis was first explored to produce O_2 for propulsion and life support in spacecraft at the National Aeronautics and Space Administration in the 1960s [3–8].

The increasing popularity of this technique is apparent based on the increasing number of articles published covering a variety of methanol synthesis via co-electrolysis. The articles have evaluated the co-electrolysis process, or reported the progress in the device, i.e., solid oxide electrolytic cell (SOEC). Some also considered the application of its co-electrolysis to PtM [9–24]. A timeline showing the published reviews and the assessment categories is given in Fig. 2.

Within the first category (co-electrolysis), Fu et al. [9] evaluated the economic potential of producing syngas and Fisher-Tropsch (FT) diesel from the co-electrolysis of steam and carbon dioxide. They also suggested the operation strategy for the high temperature co-electrolyzer. Graves et al. [10] reviewed numerous pathways to synthesize the CO_2

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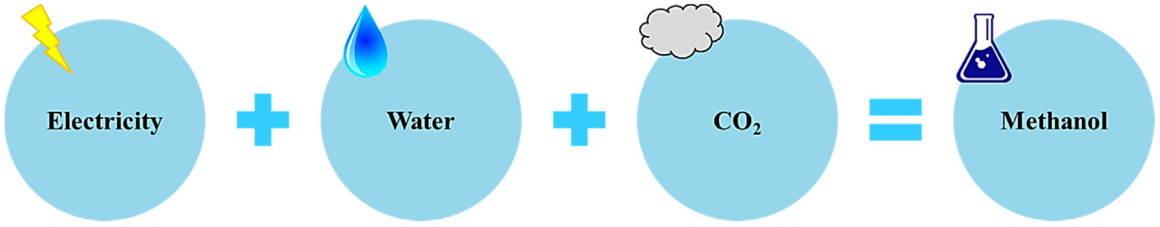
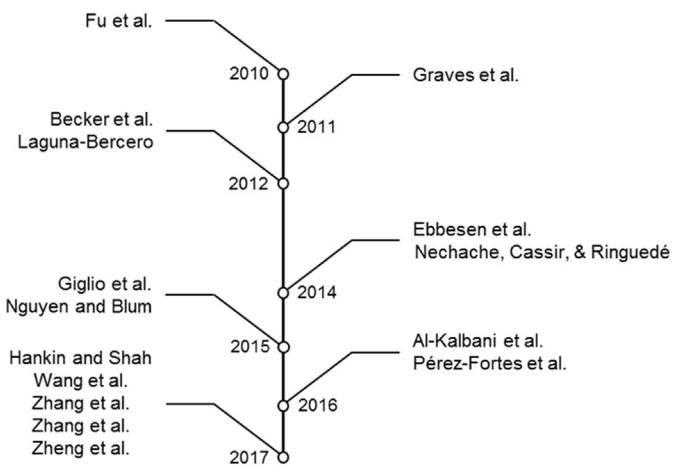


Fig. 1. The power-to-methanol concept.



	Co-electrolysis	SOEC	PtM	PtM via Co-electrolysis	References
Fu et al. (2010)	√				[9]
Graves et al. (2011)	√				[10]
Becker et al. (2012)	√	√			[11]
Laguna-Bercero (2012)		√			[12]
Ebbesen et al. (2014)		√			[13]
Nechache, Cassir, & Ringuedé (2014)		√			[14]
Giglio et al. (2015)	√				[15,16]
Nguyen and Blum (2015)	√	√			[17]
Al-Kalbani et al. (2016)	√		√	√	[18]
Pérez-Fortes et al. (2016)			√		[19]
Hankin and Shah (2017)	√		√		[20]
Wang et al. (2017)	√	√			[21]
Zhang et al. (2017)	√	√			[22]
Zhang et al. (2017)	√	√			[23]
Zheng et al. (2017)	√	√			[24]

Fig. 2. A timeline of co-electrolysis and power-to-methanol related reviews and assessments.

recycled fuels and claimed that high temperature co-electrolysis has the highest potential, with 70% efficiency from electricity to FT liquid fuels, according to their estimation based on energy and economics analysis. Giglio et al. [15,16] studied the energy performance and economics of synthetic natural gas production via two routes: (1) integrated steam electrolysis with methanation (Sabatier reaction) and (2) the co-electrolysis of water and CO_2 coupled with TREMP™ (the Topsøe recycle energy-efficient methanation process). Their results showed that synthetic natural gas (SNG) production via co-electrolysis has higher capital, operating, and maintenance costs. However, there is a weaker dependence on the electricity cost because of the higher plant efficiency.

The second category is associated with SOECs. Laguna-Bercero [12] compiled applications, performances, and material issues facing SOEC. Ebbesen et al. [13] compared the electrolysis in different types of cells, alkaline electrolysis cells, solid proton conducting electrolysis cells, and SOEC in materials and the performance. The SOEC is modeled and its combination with photovoltaic and solar heat is expected to have 80–90% efficiency. Nechache, Cassir, and Ringuedé [14] demonstrated how electrochemical impedance spectroscopy (EIS) could be used to (1) characterize electrode materials for both H_2 and O_2 electrodes, (2) study cell degradation in different configurations (symmetrical cell, single cells, and stacks), and (3) develop a qualitative and quantitative systematic SOEC analysis approach by varying parameters such as the temperature, current density, or ratio.

Because co-electrolysis and SOECs are closely related, sometimes, works related to these topics cannot be separated. The following reviews and assessments contain aspects of the first and second categories. Becker et al. [11] presented an integrated model for SOEC and FT process where syngas is converted to liquid fuels. The overall efficiency is estimated to be 54.8% HHV and the production costs to be 4.4–15.0$/GGE (Gasoline Gallon Equivalent). Nguyen and Blum [17] reviewed the processes involved in the production of syngas and synfuels. From their study, solid oxide electrolyzer still has the challenge in developing the durable high performance cells, so that they also presented the alternative technologies for synfuels. Wang et al. [21] gave a detailed review on the thermodynamic and electrochemical principles of SOEC and the comprising materials. Ni-based cermets (metal-ceramics) was found to be common for SOEC cathode with high performance whereas its stability and durability needs to be further enhanced. Zhang et al. [22] indicated that some challenges are remained for SOEC operating at intermediate temperatures that can be resolved by developing the new materials with higher reliability with the new preparation methods. Zhang et al. [23] reviewed the development of new cathode materials for SOECs, such as the perovskite materials, and the key factors for high-performance cathode design. Zheng et al. [24] gave a detailed overview of CO_2/H_2O co-electrolysis in SOEC operated at high temperatures, illustrating thermodynamic parameters, kinetics, materials and the technological issues involved. They also concluded the research on the fundamentals and materials SOEC should be extensively followed for the success of CO_2 conversion.

In the third category, Pérez-Fortes et al. [19] simulated and assessed the economics of a methanol synthesis in a reactor which was integrated with a CCU process, in an effort to develop an economically viable model. The CO_2 conversion was 22% in the reactor, and 97% of CO_2 was converted to methanol in the overall process. 1.23 t of CO_2 could be converted to a ton of methanol according to their results. Using process modeling, Al-Kalbani et al. [18] modeled the methanol production processes from water electrolysis and CO_2 hydrogenation also integrated with a CO_2 capture process based on MEA. The process is then compared with a high-temperature SOEC process. The overall energy consumption was lower by 49%, thereby the energy efficiency was the twice higher for the SOEC process. Hankin and Shah [20] evaluated four different systems for producing methanol of dimethyl ether from CO_2 in simulations. From the result, they suggested to produce methanol from syngas, which was synthesized in high temperature electrolyzers. They also indicated that an alkaline water electrolyzer combined with a RWGS system was less preferred for methanol