17th International Conference on Inorganic Membranes
New Frontiers for Inorganic Membranes
July 1 - 5, 2024
Oceania Convention Center - Florianópolis - Brasil

CO_2 electro-catalytic reduction into CH_4 in a pressurized protonic electrochemical membrane reactor

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Abstract

Electrochemical membrane reactors can improve the energy efficiency of chemical reactions, such as producing synthetic fuels, by coupling exothermic and endothermic processes. This work, developed in the frame of the EU Horizon 2020 "eCOCO2" project, presents the CO_2 electro-catalytic reduction into methane by using tubular protonic membrane reactors. Two different modes of operation were employed to provide the needed H_2 for the methanation reaction: H_2 pumping and electrolysis. In both operation modes, the protonic membrane was composed of $BaZr_{0.8}Ce_{0.1}Y_{0.1}O_3$ as electrolyte and the cermet $Ni+BaZr_{0.7}Ce_{0.2}Y_{0.1}O_3$ as inner metallic electrode acting as support and as methanation catalyst[1]. In the case of the H_2 pumping, the outer electrode was made of $Ni+BaZr_{0.7}Ce_{0.2}Y_{0.1}O_3$, whereas for the electrolysis, an electrode made of $PrBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O_{5+\delta}$ (PBSCF) was used.

Transport properties of electrochemical cells were evaluated using impedance spectroscopy, i-V curves, and H2 production under varying current densities and operational conditions, from 600 °C to 450 °C and pressures up to 30 bar. Then, methanation reaction performance was also evaluated as a function of the operational parameters, analyzing the CO_2 conversion and CO and CH_4 yields.

In both operational modes, it was observed that the total system pressure plays a key role in both the electrochemical and catalytic performances of the protonic cells.[2] The DRT analysis inferred that the improvement in high-pressure performance is due to two simultaneous effects.: (i) increased hydration of the electrolyte, which enhances the proton conductivity, and (ii) the improvement of the surface kinetics and mass, transfer of the electrodes. Regarding catalytic performance, CO_2 conversion, and CH_4 selectivity increase significantly with pressure, reaching values of 86% and 94%, respectively, for a stoichiometric H_2/CO_2 ratio of 4 at 450 °C and 30 bar.

In addition, computational fluid dynamics (CFD) simulations were conducted to gain critical insights into the reaction kinetics, transport phenomena, and electrochemical performance of the membrane reactor.

Acknowledgment: This study has received European Union's Horizon 2020 Research and Innovation funding under grant agreement No 838077. CoorsTek Membrane Sciences is gratefully acknowledged for their assistance in the manufacture of tubular cells.

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