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Project Title : Development of catalyst-impregnated metal-foam supported solid oxide electrolysis cell combined with hydrogen separation membrane for hydrogen and syngas production from carbon dioxide and steam integrative with alcohol-assisted methanol synthesis from carbon dioxide and hydrogen

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Abstract

There are two platforms of the work from this research: **1)** hydrogen (H_2) and syngas production from steam and carbon dioxide (CO_2) through solid oxide electrolysis cell (SOFC) and **2)** methanol production from carbon dioxide and hydrogen through alcohol-assisted method. The connection between both research platforms is the idea that hydrogen or syngas produced from the first platform can be utilized in the second research platform.

For the first platform, solid oxide electrolysis technology has been developed. The research in this platform has been divided into two focus: **1.1)** improving chemical stability of SOEC and **1.2)** improving fabrication of SOEC. The second research platform presents the correlation between Cu/ZnO catalyst preparation conditions on the catalyst properties and activity in methanol synthesis from CO_2 and H_2.

For the first research platform - improving chemical stability of SOEC, proton conductor material has been synthesized. Effect of strontium and zirconium doped barium cerate on the performance of proton ceramic electrolyser cell for syngas production from carbon dioxide and steam has been studied. Syngas has been produced from carbon dioxide (CO_2) and steam using a proton ceramic electrolyser cell. Proton-conducting electrolytes which exhibit high conductivity can suffer from low chemical stability. In this study, to optimize both proton conductivity and chemical stability, barium cerate and doped barium cerate are synthesized using solid state reaction method: $BaCeO_3$ (BC), $Ba_{0.6}Sr_{0.4}CeO_{3-\alpha}$ (BSC), $Ba_{0.6}Sr_{0.4}Ce_{0.9}Y_{0.1}O_{3-\alpha}$ (BSCY), and $BaCe_{0.6}Zr_{0.4}O_{3-\alpha}$ (BCZ). The BC, BSC, and BSCY are calcined at 1100°C for 2 h and BCZ is calcined at 1300°C for 12 h, respectively. All samples exhibit 100% perovskite and crystallite sizes equal 37.05, 28.46, 23.65 and 17.46 nm for BC, BSC, BSCY and BCZ, respectively. Proton conductivity during steam electrolysis as well as catalytic activity toward the reverse water gas shift reaction (RWGS) is tested between 400 and 800°C. The conductivity increases with temperature and the values of activation energy of conduction are 64.69, 100.80, 103.78 and 108.12 kJ mol^{-1} for BSCY, BC, BSC, and BCZ, respectively. It is found that although BCZ exhibits relatively low conductivity, the material provides the highest CO yield at 550-800°C, followed by BSCY, BSC, and BC, correlating

to the crystallite size and BET surface area of the samples. Catalytic activity toward RWGS of composited Cu and electrolytes is also measured. Additional Cu (60 wt.%) significantly increases catalytic activity. The CO yield increases from 3.01% (BCZ) to 43.60% (Cu/BCZ) at 600°C and CO can be produced at temperature below 400°C. There is no impurity phase detected in BCZ sample after exposure to CO_2-containing gas mixture (600°C for 5 h) while CeO_2 phase is detected in BSC and BSCY and both CeO_2 and BaO are observed in BC sample.

For the second research platform - improving fabrication of SOEC, the effect of sintering additives (NiO, Co_2O_3, and ZnO) on the performance of barium-cerate-based solid oxide electrolysis cell (SOEC) is investigated. The performance of the SOEC with different sintering additives is determined in terms of relative density, electrochemical performance, and catalytic activity toward reverse water gas shift reaction. $BaCeO_3$ (BC) and $BaCe_{0.9}Gd_{0.1}O_{3-\delta}$ (BCG) are synthesized using conventional precipitation method, comparing to ultrasonic-assisted precipitation. The sintering additives promote both densification and grain growth. The relative density of the BCG without sintering additive is 69% while that of the BCG with 1 wt.% of Co_2O_3, NiO and ZnO is 95%, 95% and 88%, respectively. The SEM images indicate that the BCG with sintering additives exhibits dense grains with relatively large grain size. Although the BGC with NiO and Co_2O_3 exhibit maximum relative density, the sample with ZnO shows relatively highest conductivity with the lowest activation energy of conduction and the sample with NiO provides the largest CO yield and CO_2 conversion. The activation energy of conduction is found to be 375.41, 70.06, 66.86 and 61.80 $kJmol^{-1}$ for BCG, BCG with 1 wt.% Co_2O_3, NiO and ZnO, respectively. The BCG with 1 wt.% NiO provides the highest CO_2 conversion and CO yield at temperature below 700°C (62% CO_2 conversion and 32% CO yield at 700°C). Temperature program of oxidation (TPO) reveals that carbon deposition can cause the low CO yield at the operating temperature above 700°C.

For the second research platform – synthesize of methanol from CO_2 and H_2 through alcohol assisted method, CuO/ZnO catalysts are synthesized using a co-precipitation method with different precipitation temperatures (298-353 K) and pH values (5-9). A conventional precipitation is compared to an ultrasonic-assisted precipitation at

each precipitating temperature. Methanol is directly synthesized from CO_2 and H_2 (1:3 mol ratio) through an alcohol-assisted reaction (423 K, 5 MPa, 24 h) by using different alcohols (ethanol, propanol and butanol) as a medium. There are two parts for the challenge of this research, including the preparation of CuO/ZnO catalysts using an ultrasonic-assisted precipitation and, methanol synthesis through an alcohol-assisted method. It is found that the precipitation temperature and pH value significantly affect the catalyst properties and the reaction activity. An ultrasonic irradiation helps facilitate the crystalline phase formation and decrease precipitation temperature. The highest yield of methanol is obtained when CuO/ZnO is precipitated at 333 K from the conventional precipitation (31%) while it is at 313 K from the ultrasonic-assisted precipitation (32%). In addition, the different type of alcohol strongly affects methanol yield and CO_2 conversion. The use of larger alcohol molecules offers higher CO_2 conversion but lower methanol yield.