Parametric optimization and kinetic analysis of CO_2 hydrogenation in SOEC: A step further towards power to X

Erum Pervaiz[1]*, Ronny Monnig[1], Kevin M. Van Geem[1]

1 Laboratory of Chemical Technology (LCT), Gent University, 9200 Gent, Belgium

**Corresponding author: erum.pervaiz@ugent.be*

Highlights

- Co-electrolysis of steam and CO_2 on Ni-YSZ supported fuel electrodes at 800°C.
- Over potentials of CO_2 rich feed observed to be much lower than H_2 rich feed.
- Surface kinetics played vital role contributing towards Faradaic efficiency at 800°C.

1. Introduction

Decarbonization and energy are two main challenges needs to be addressed importantly and points towards modern technologies that could mitigate both at the same time. Sold oxide technology is considered efficient and thermodynamically more viable for CO_2 conversion and use of renewable energy to produce clean fuel with zero C footprint. This technology can offer co-electrolysis of steam and CO_2 producing syngas at much faster rate and desired ratio of H_2/CO. Although stability and durability is a bottleneck to the commercialization but energy efficiency and high power density makes this technique most reliable at the moment comparable to other green fuel production methods. High Temperatures beyond 700°C offers thermochemical conversion of CO_2 via RWGS reaction producing a lot of water that can be electrolyzed in the SOECs. At the same time CO_2 is electrolyzed to CO producing more CO via fuel assisted electrolysis in the cells. This work offers a detailed analysis of CO_2 hydrogenation as a starting mixture yielding a fuel composed of CO_2, CO, H_2 and H_2O, that is electrolyzed within the cells at a constant temperature of 800°C. The Faradaic efficiency (FE) of this fuel assisted electrolysis found to be dependent upon the inlet feed ratio of H_2/CO_2.

2. Methods

Custom made in house designed Ni-YSZ supported cells are used with $La_{0.7}Sr_{0.3}MnO_3$ air electrode and 8-YSZ as electrolytes. A stack with two layers of cells 5x5cm^2 with active area of 12 cm^2 is used in the study. Electrode thickness are 400µm|10µm|50µm were used in the study. 7 different inlet feed ratios of H_2/CO_2 namely 8.0, 5.66, 4.0, 2.83,2,1 and 0.5 are considered for the study. A function generator and amplifier is used to study the current voltage and impedance analysis. Impedance results were fitted to the model by the MATLAB code.

3. Results and discussion

The work includes H_2 rich feeds to H_2 lean mixtures (H_2/CO_2=8 to 0.5) and the effect of various parameters are studied such as overpotentials, Tafel slopes, Exchange current density, activation and polarization resistances. Fig. 1 (a) presents the composition of fuel at open cell voltage (I=0) for different H_2/CO_2 ratios at 800°C as a result of RWGS reaction. The equilibrium conversion of CO_2 at 800°C Vs the actual conversion of CO_2 is presented in Fig 1 (b) which shows a variation in conversion based upon the ratio of H_2/CO_2 of the cold inlet. The comparison of thermodynamic equilibrium and actual equilibrium (partial pressure dependent) is also presented in the same figure. The H_2 lean mixture showed the fraction more close to 1. Fig 1 (c) shows the partitioning factor (dimensionless number used to divide the FE) of electrolysis. Whereas FE of CO_2/CO and H_2O/H_2 (two co-electrolyzing species) is shown in figure 1 (d). It is clearly observed that FE of total reaction is always 100%. Furthermore the surface reaction based mechanism is used to fit the experimental data to provide more insights and support to the kinetics of co-electrolysis reaction on Ni-YSZ supported cells. J-V curves of the cells showed a linear ohmic behavior depicting no concentration polarization exist and contributed towards the over potential. The minimum overpotential of 17 mV is observed for H_2 lean mixture ($H_2/CO_2=1$) with exchange current density of 0.781 A/cm^2 and polarization resistance of 0.27 (Ω -cm^2). The effect of residence time (0.25 sec and 0.5sec) is further considered and found to be important effecting the RWGS and surface kinetics during electrolysis. At 800 °C and an applied voltage of 2.7 V, the impedance response of the SOEC varied systematically with the inlet H_2/CO_2 ratio. The polarization resistance (Rp) decreased progressively as the feed shifted from H_2-rich (H_2/CO_2 = 8–6, Rp ≈ 2.9–3.3 Ω-cm^2) to CO_2-rich conditions (H_2/CO_2 = 1–0.5, Rp ≈ 0.6–0.27 Ω). Power density of 0.471 W/cm^2 and 0.453 W/cm^2 is obtained at 0.21 A/cm^2 for 0.25 sec and 0.5 sec of residence times respectively. Maximum current density of 0.8A/cm^2 is observed for residence time of 0.25 sec at 800°C and reactor voltage of 1.4 V. Meanwhile an overall FE of 96%-100% is achieved for all the inlet feed ratios at 800°C. This study presents an important analysis for enhancing the power density and current density of SOEC for syngas production.

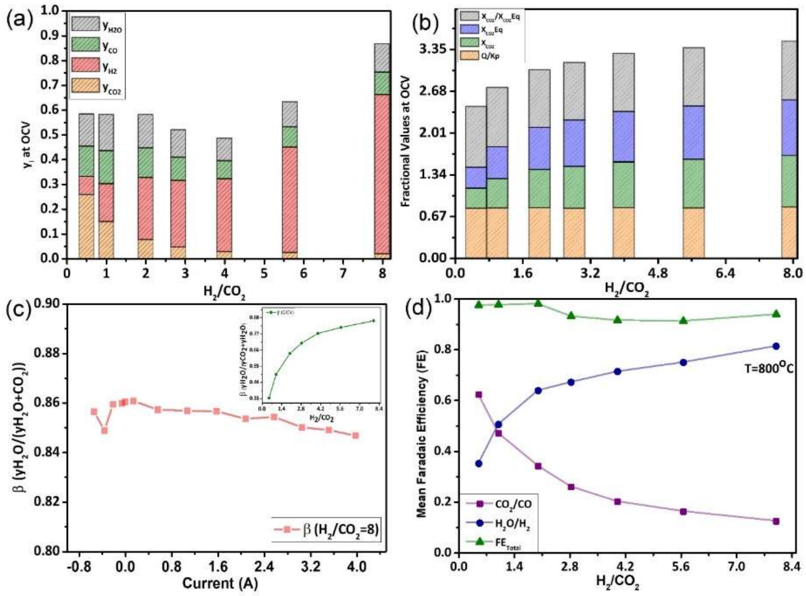

Figure 1. (a) Fuel composition for various feed inlet at open cell voltage (OCV) before electrolysis (b) Fractional values of thermodynamic equilibrium Kp, fuel quotient (Q), equilibrium CO_2 conversion, actual CO_2 conversion and their ratio for all the feed inlet ratios at OCV (c) partitioning factor during co-electrolysis (inset) partition factor with H_2/CO_2 ratio(d) FE of CO_2/CO and H_2O/H_2 electrolysis at 800°C

4. Conclusions

Anode supported Ni-YSZ cells are efficiently used for syngas production at 800°C. Various parameters are optimized and kinetics is studied with effect to inlet concentration of cold feed (H2/CO2). Effect of flow rate/residence time is also considered and found to be important to achieve desired current and power density.

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Keywords

Co-electrolysis; SOEC; syngas; green fuels