Electronic Supplementary Information (ESI)

Power-to-gas Systems Utilizing Methanation Reaction in Solid Oxide Electrolysis Cell Cathodes: A Model-based Study

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Pressure dependence of exchange current densities

Partial pressure dependence of exchange current densities has been examined in the field of SOFC (solid oxide fuel cell). It is reasonable to apply the values obtained in the SOFC studies to SOEC simulations because exchange current densities represent the rate of reversible reaction at open circuit conditions. In most cases, the partial pressure dependences are examined in a range of 0-1 atm, and expressed by the following formulae:

$$i_{0,H_2} = \gamma_{H_2}\left(\frac{p_{H_2}}{p_{std}}\right)^A\left(\frac{p_{H_2O}}{p_{std}}\right)^B \exp\left(-\frac{E_{a,H_2}}{RT}\right)$$

$$i_{0,CO} = \gamma_{CO}\left(\frac{p_{CO}}{p_{std}}\right)^C\left(\frac{p_{CO_2}}{p_{std}}\right)^D \exp\left(-\frac{E_{a,CO}}{RT}\right)$$

Here we focus on the exponents A-D. Table S1 summarizes the values reported in the literature. The results differ significantly, possibly due to the cell geometries and test conditions. The value of A+B obtained from Table S1 ranges from 0.23 to 3.

Table S1. Reported pressure dependence of exchange current densities (0-1 atm).

Reference	Year	Electrode	A	B	C	D	Note
[1]	1993	Ni-YSZ	1	1			Low p_{H2}
			2	1			High p_{H2}
[2]	1994	Ni pattern	0	1			$p_{H2O} >> p_{H2}$
			0.5	0			$p_{H2O} << p_{H2}$
[3]	1999	Ni-YSZ	0.1	0.5			
[4]	2009	Ni-YSZ	-0.10	0.33			
[5]	2011	Ni-YSZ			-0.058	0.25	
[6]	2011	Ni-ScSZ	0.41	0.40			

It is noted again that most of the previous researches explored the pressure dependence in the range of 0-1 atm. Only a few experimental data are available for the pressure dependence at operating pressures higher than 1 atm. Matsui *et al.*[7] performed an impedance analysis in a total pressure range of 100-300

kPa, and suggested that the results were consistent with the partial pressure dependence reported by Mizusaki *et al.*[2] even at elevated pressures. Kikuchi *et al.*[8] reported impedance spectra measured at different H_2 or H_2O partial pressures in a range of 0-10 atm. According to the spectra, it is qualitatively assumed that the exponent A is around zero while the exponent B is positive. However, further quantitative analysis is still needed to determine the dependences at high pressures. Kazempoor and Braun[9,10] performed simulations of pressurized solid oxide cells by applying the equations developed for near atmospheric pressure conditions. They pointed out that more activities are necessary to check the validity of those equations for pressurized operation[10].

References

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Simulation results in the case of A+B = 2

In the present study, we consider the pressure dependence of the cathode exchange current densities by using A+B as a parameter. Here we show the simulation results obtained by assuming A+B = 2. Even though the individual results are different from those in the A+B = 0.25 case exhibited in the main article, the trends of the results are shared.

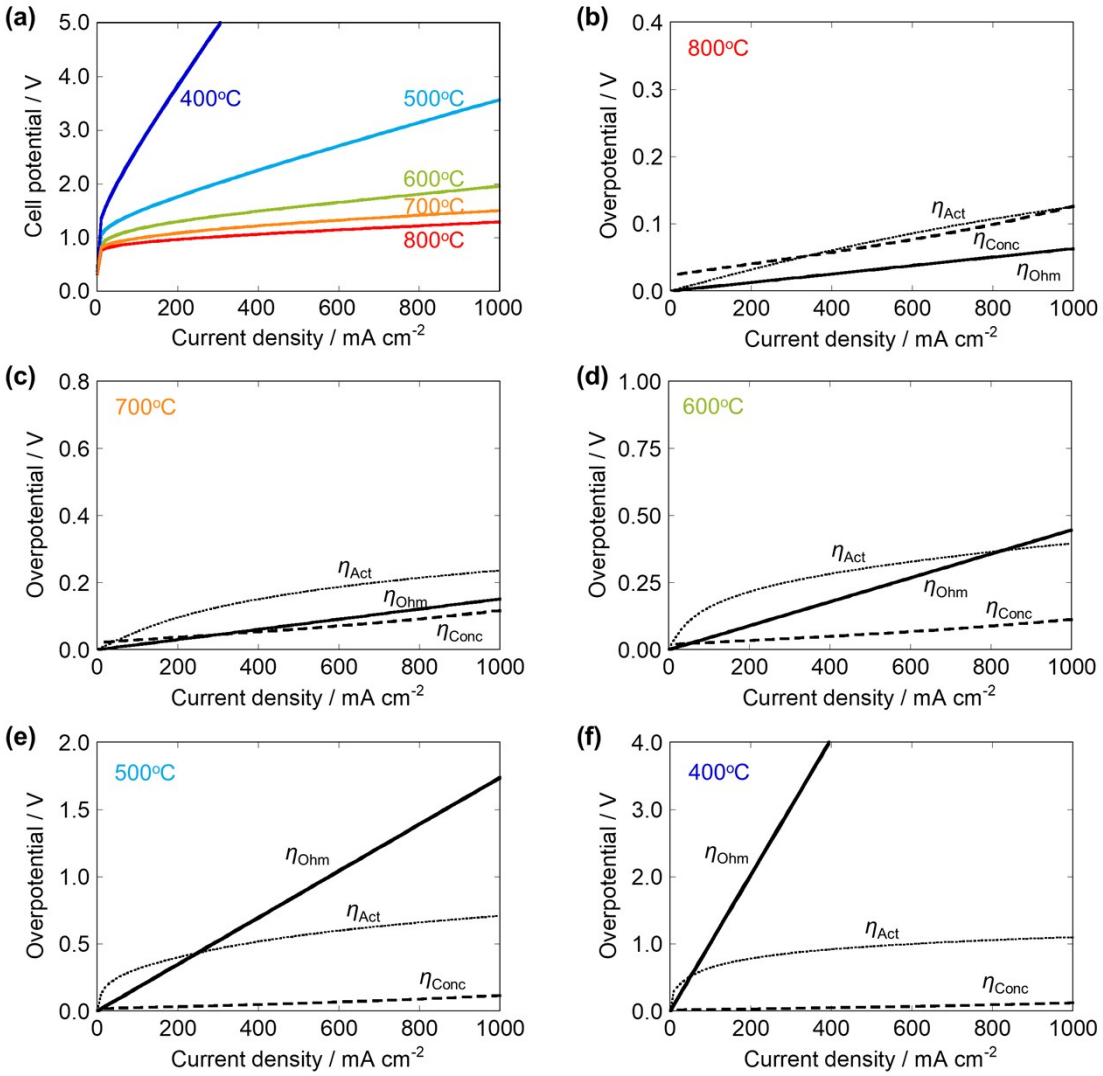

Fig. S1 [A+B = 2] (a) Current-voltage characteristics of the SOEC unit at 400°C-800°C, 5 atm. (b)-(f) Breakdown of the overpotentials at each temperature. This figure corresponds to Fig. 7.

The pressure dependence of the cathode exchange current densities is stronger in this case, resulting in the smaller activation overpotentials.

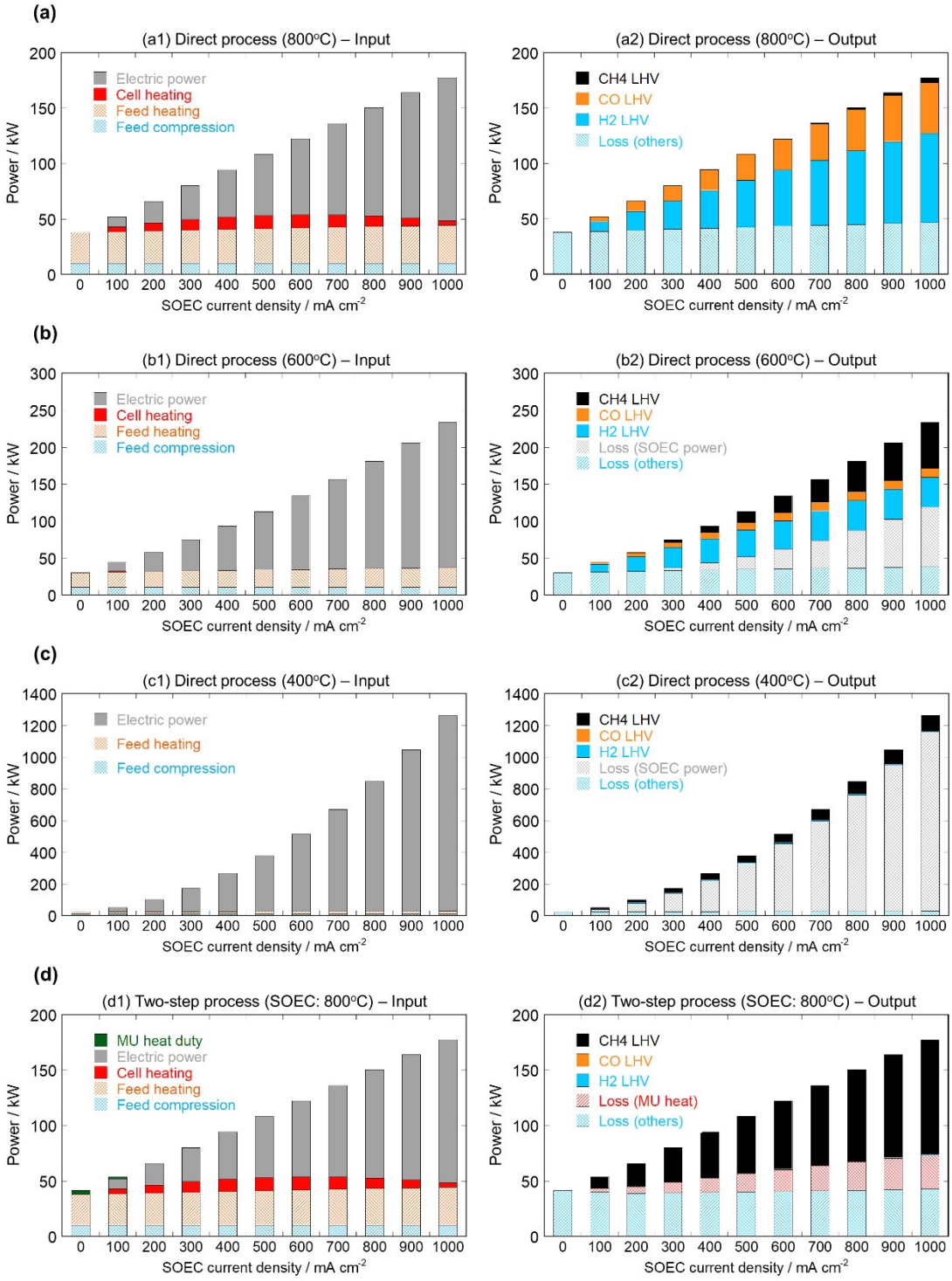

Fig. S2 [A+B = 2] Details of the energy input and output of the examined power-to-gas systems. SOEC operating pressure is 5 atm. This figure corresponds to Fig. 8.

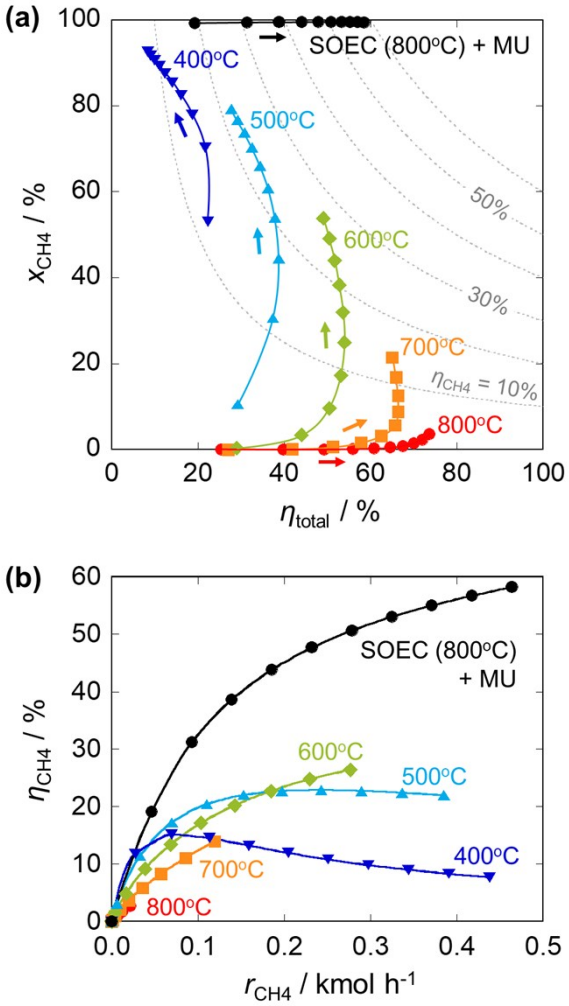

Fig. S3 [A+B = 2] Energy conversion efficiencies of simulated systems. (a) $^{x_{CH_4}}$ vs. $^{\eta_{total}}$ plot, (b) $^{\eta_{CH_4}}$ vs. $^{r_{CH_4}}$ plot. Data corresponding to SOEC current density of 0-1000 mA cm^{-2} are shown. SOEC operating pressure is 5 atm. This figure corresponds to Fig. 9.

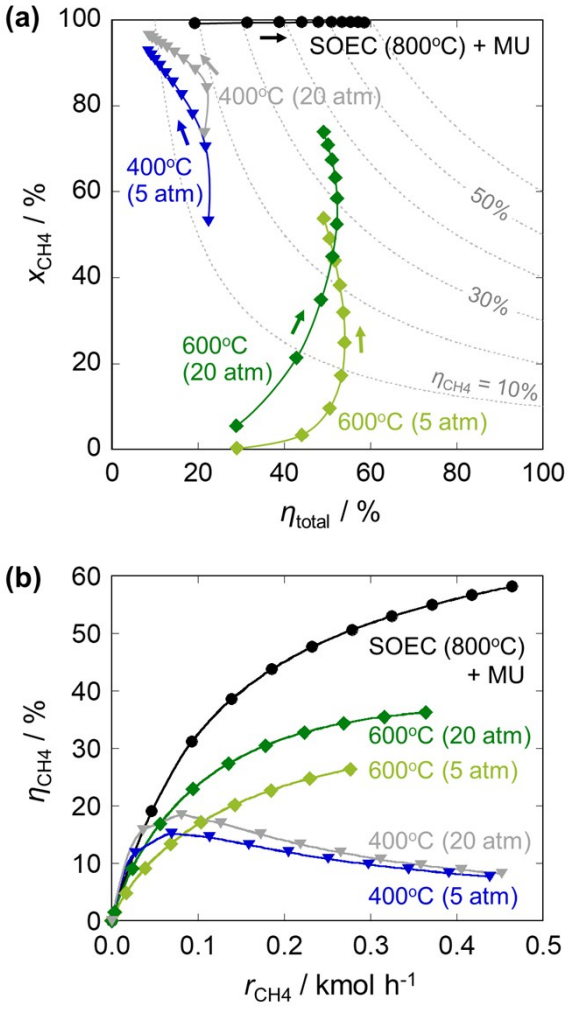

Fig. S4 [A+B = 2] Effects of operating pressure of the direct process on energy conversion efficiencies: (a) $^{x_{CH_4}}$ vs. η_{total} plot, (b) $^{\eta_{CH_4}}$ vs. $^{r_{CH_4}}$ plot. Data corresponding to SOEC current density of 0-1000 mA cm^{-2} are shown. This figure corresponds to Fig. 12.