Supporting Material for

Roles of Reaction Kinetics of CO_2 on a $PrBaCo_2O_{5.5+\delta}$ Surfaces

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The splitting of carbon dioxide is a challenging topic. Many efforts have been performed to achieve the reduction and conversion of the CO_2. One of the direct conversion techniques is the splitting of CO_2 into CO and O2. Various materials are explored to achieve this goal. For comparison, some novel results from the previous research are listed in Table S1

Table S1 the current status of the CO2 splitting techniques and materials

Technique	Material	Reactant	Temperature(^oC)	Ea(eV)
Symmetric cell (This work)	PrBCO/YSZ/PBCO	CO2	700~900	1.1, k_{chem}
Solid electrolysis cell	LSCM/YSZ, LSCM/GDC[1]	CO2/CO	900	NA
Solid electrolysis cell	(La,Sr)(Cr,Mn)O3/GDC[2]	CO2/CO	900	NA
Solid electrolysis cell	Cu/CGO[3]	CO2/CO=1:1	750	NA
Solid electrolysis cell	Ni/YSZ[4]	CO2/CO=1:1 et al	850	NA
Solid electrolysis cell	$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}-Gd_{0.1}Ce_{0.9}O_{2-\delta}$ (LSCF6428–GDC)[5]	CO2/H2O	700-850	0.7, R_{total}
Solid electrolysis cell	La0.2Sr0.8TiO3[6]	CO2	700	NA
Thermalchemical	La1xCaxMnO3 (LCM)[7]	H2O, CO2	1300	NA
Two step thermalchemical	Ce1-xZrxO2[8]	CO2	800–1050	NA
Two step thermalchemical	LaFeO3/IrOx[9]	CO2	900-1100	2.27, Resistance

Our results indicate that the operation temperature can be as low as around 700~900°C with small activation energy 1.1eV for surface exchange coefficient k_{chem}. This is much lower than many other materials for the pure CO_2 reduction, such as 2.27eV activation energy for LaFeO3/IrOx and with high operation temperature. Although LSCF6428-GDC[5] shows lower 0.7eV activation energy than PBCO, it required the reaction in the CO_2/H_2O mixture. For the pure CO_2 reduction, the result of this context is most advanced.

The EIS measurement in CO_2 has low oxygen partial pressure and the PrBCO electrodes will lose oxygen content in heating process.[10] The oxygen content changes because of the low oxygen partial pressure in the CO_2 ambient at high temperature. We note that the value of x in $PBCo_2O_{5.5+x}$ is proportional to the log scale of the oxygen partial pressure,[11] and that at a lower oxygen partial pressure the oxygen content of a perovskite oxide decreases.[12]

In the as-grown PBCO thin film electrode, large number of oxygen vacancies exist and the oxygen stoichiometry deviate from fully oxidized state. When the PBCO electrode is heating up in the carbon dioxide ambient, the oxygen vacancies in the lattice are activated and the stoichiometry is changed due to the oxygen ions and species provided by the splitting of the carbon dioxide on the electrode surface. The oxygen stoichiometry strongly alters the chemical catalysis performance of the PBCO electrode. In the main part of this research, the latter two cycles show same shapes in the surface resistance Rs, surface capacitance Cs, interface resistance Ri and the surface exchange coefficient k_{chem}. In Fig. S1, the fitting result of the 1st cycle after the installation of the symmetric cell are demonstrated. The diagram of surface resistance Rs, the value increases with the temperature monotonically and shows a slope transition near 1073K. Similar transitions exist in surface capacitance Cs, electrode electrolyte interface resistance Ri and the surface exchange coefficient. Meanwhile, this kind of transitions doesn't exist in the following cycles which the oxygen vacancies are rebalanced in the carbon dioxide ambient. This transition behavior can be described that the equilibrium between the oxygen partial pressure provided by the splitting of carbon dioxide and that inside the PBCO electrode. In the 1st cycle, PBCO electrode is heat up from room

temperature to 973K and the oxygen provided by carbon dioxide is limited due to the high reaction activation energy. Thus the as-grown fully oxidized PBCO lost oxygen to the ambient till to the equilibrium oxygen stoichiometry. This process only exists in the first cycle and demonstrates unique shape comparing to the results of the other two processes. Then heat up to higher temperature, PBCO electrode can obtain the oxygen in the first cycle as in the other two cycles.
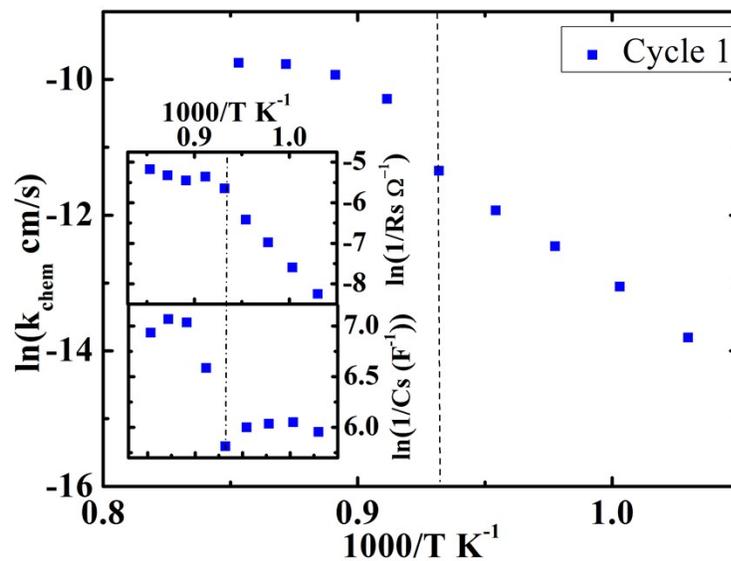
Figure S1. The fitting results of the cycle 1. The dash line is the 800°C and where a transition happens.

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