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Electronic Supplementary Information

Direct biofuel low-temperature solid oxide fuel cells

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Preparation of electrolyte and electrode

The electrolyte for investigation was samarium doped ceria-sodium carbonate composite (NSDC) electrolyte prepared by carbonate co-precipitation method. Firstly, $Ce(NO_3)_3{\cdot}6H_2O$ (99.99%, Sigma–Aldrich) and $Sm(NO_3)_3{\cdot}6H_2O$ (99.9%, Sigma–Aldrich) were dissolved in deionized water with a stoichiometric molar ratio of Ce^{3+}: Sm^{3+}=4:1 to obtain a 100 ml solution (the molar concentration of the total rare-earth metal cation ion is 1.0 M). Then 200 ml of Na_2CO_3 solution (1.0 M) was added slowly (with a flow rate of 10 mL min^{-1}) into the solution under vigorous stirring to form a white precipitation at room temperature. After stirring for 2 h, the precipitation was filtered by suction traction method and dried in the oven over night at 50 ^oC. Finally, the NSDC precursor was crushed and sintered at 800 ^oC for 2 h.

The $Li_{0.2}Ni_{0.7}Cu_{0.1}O$ catalyst was prepared by a sol-gel reaction. A stoichiometric amount of Li_2CO_3 (99.99%, Sigma–Aldrich), $CuCO_3{\cdot}Cu(OH)_2$ (95%, Sigma–Aldrich) and $NiCO_3{\cdot}2Ni(OH)_2{\cdot}4H_2O$ (~46% Ni basis, Sigma–Aldrich) were mixed and dissolved in deionized water to form a 1.0 M solution. Then the solution was added with citric acid (99.5%, Sigma–Aldrich) in a molar ratio of total metal cation ion: citric acid=1:2 and stirred vigorously to obtain a homogeneous solution. The obtained solution was heated with continuous stirring at 100 ^oC for 2 h to form a glassy sol. Finally, the obtained sol was sintered in air at 800 °C for 2 h resulting in the $Li_{0.2}Ni_{0.7}Cu_{0.1}O$ catalyst.

Equal volume of NSDC powder and $Li_{0.2}Ni_{0.7}Cu_{0.1}O$ catalyst powder were first mixed and ground to prepare anode and cathode materials. NSDC was used as the electrolyte material. The cathode, electrolyte and anode were uniaxially pressed into a cylindrical pellet by a hot co-pressed process at 600 °C under 100 MPa. The pellets had diameter of 20 mm and thickness of 1 mm. Finally, both anode and cathode surface were covered with silver mesh as current collectors for fuel cell performance measurements..

Evaluation of cell performance and catalyst

A single fuel cell with the active area of 2 cm^2 was assembled to evaluate the cell performance of the biofuel used in the low temperature solid oxide fuel cell. The solutions of the feed biofuel (market-bioethanol, 56 wt.%, Beijing Redstar Co., Ltd.; glycerol, 85 wt.%, Apoteket Produktion & Laboratorier AB) in deionized water with a mass concentration of 50 wt.% were used as the fuels. The cell tests were carried out under a fuel solution flow rate of 1.0 mL min^{-1}, a reforming gas flow rate of 100 mL min^{-1} and a dry air flow rate of 100 mL min^{-1} under 1 atm pressure. The temperature of the reforming reactor is 600 ^oC and the operation temperature of the fuel cell is 580 ^oC. The electrochemical performance of the fuel cell was measured by a computerized instrument (L-43). The crystal structure of catalyst was identified by X-ray diffraction with Rigaku-D/Max-3A diffractometer using Cu Kα radiation (λ = 1.5406 Å). The surface of anode before and after operating was investigated by a Zeiss Ultra 55 field-emission scanning electron microscope combined with an energy-dispersive X-ray spectroscopy.

Thermodynamic parameters for calculation of theoretical open circuit voltage (OCV)

Reactions:

$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O \quad \text{(overall)} \qquad (1)$$

$$C_3H_8O_3 + \frac{7}{2}O_2 \rightarrow 3CO_2 + 4H_2O \quad \text{(overall)} \qquad (2)$$

Tab. S1 Thermodynamic parameters for calculation of theoretical open circuit voltage (OCV).

Compounds	C_2H_5OH(l)	$C_3H_8O_3$(l)	O_2(g)	CO_2(g)	H_2O(l)
$\Delta_f G^0$(kJ mol^{-1})	−174.8	−476.5	0	−394.4	−237.1
S^0(J $K^{-1}mol^{-1}$)	160.7	206.3	205.1	213.8	70

* Data from CRC Handbook of Chemistry and Physics and Lange's Handbook of Chemistry

According to the Nernst equation,

$$E = \frac{\Delta G^0}{nF} \qquad (3)$$

Where the ΔG^0 is the Gibbs free energy change of the reaction, n is the number of electronic of the reaction, F is Faraday constant (96485 C mol^{-1}). Therefore, the OCV of reaction 1 and reaction 2 can be calculated as follows,

$$\text{OCV}_{\text{ethanol}} = -\frac{(3\times 237.1 + 2\times 394.4\text{-}174.8)\times 1000}{12\times 96485} = 1.14 \text{ V}$$

$$\text{OCV}_{\text{glycerol}} = -\frac{(4\times 237.1 + 3\times 394.4\text{-}476.5)\times 1000}{14\times 96485} = 1.22 \text{ V}$$

According to the relationship between the theoretical OCV and temperature,

$$E_T = E^0 + \frac{\Delta\hat{s}}{nF}\left(T - T_0\right) \quad (4)$$

where E_T is the theoretical potential for the cell at the temperature of T, E^0 is the theoretical standard potential of the cell, $\Delta\hat{s}$ is the entropy change of the reaction.

When estimating the E_T, the $\Delta\hat{s}$ is usually assumed to be equal to $\Delta\hat{s}^0$. Therefore, the OCV of reaction 1 and reaction 2 at the operation temperature of 580 ^{o}C can be calculated as follows,

$$\mathrm{OCV}_{\mathrm{ethanol}}\left(580\ ^{o}\mathrm{C}\right) = 1.14 + \frac{-138.4}{12 \times 96485}\left(853.15 - 298.15\right) = 1.074\ \mathrm{V}$$

$$\mathrm{OCV}_{\mathrm{glycerol}}\left(580\ ^{o}\mathrm{C}\right) = 1.22 + \frac{-2.75}{14 \times 96485}\left(853.15 - 298.15\right) = 1.219\ \mathrm{V}$$