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ARTICLE

$\text{La}_{0.4}\text{Sr}_{0.6}\text{Co}_{0.7}\text{Fe}_{0.2}\text{Nb}_{0.1}\text{O}_{3-\delta}\text{-Gd}_{0.2}\text{Ce}_{0.8}\text{O}_{2-\delta}$ as Symmetrical Electrode Material for Reversible Solid Oxide Cells

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Abstract: $\text{La}_{0.4}\text{Sr}_{0.6}\text{Co}_{0.7}\text{Fe}_{0.2}\text{Nb}_{0.1}\text{O}_{3-\delta}\text{-Gd}_{0.2}\text{Ce}_{0.8}\text{O}_{2-\delta}$ (LSCFN-GDC) with high catalytic performance was synthesized by one-step co-synthesis method for developing a symmetrical reversible solid oxide cell (SOC) electrode. Electrolyte-supported symmetrical SOCs were fabricated by tape-casting and screen-printing methods with $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.83}\text{Mg}_{0.17}\text{O}_{3-\delta}$ (LSGM) as the electrolyte and LSCFN-GDC as both anode and cathode. The configuration of SOC is LSCFN-GDC||LSGM||LSCFN-GDC. Solid oxide fuel cell (SOFC) and solid oxide electrolysis cell (SOEC) modes were used to test the performance of SOCs. The results show that the maximum power densities are 1.036, 0.996, 0.479, and 0.952 W/cm² under the atmosphere of fuel gas of H₂ (3% H₂O), H₂ (0.01% H₂S), CH₄, and C₃H₈ at 850 °C, respectively. The current density at the electrolytic voltage of 1.3 V is 0.943 A/cm² during the electrolysis of H₂ (50% H₂O). LSCFN-GDC has good coking-resistance, sulfur-tolerance, and redox stability, and its stable performance can be sustained for 700 h under the atmosphere of H₂ (0.01% H₂S), CH₄, H₂ (3% H₂O), and H₂ (50% H₂O). The results indicate that the one-step method is a facile and optimized fabrication procedure of electrode and LSCFN-GDC||LSGM||LSCFN-GDC SOCs have great potential in further application.

Key words: LSCFN-GDC symmetrical electrode; reversible solid oxide cells; coking-resistance; sulfur-tolerance

At high temperatures, solid oxide fuel cells (SOFCs) can directly convert the chemical energy of fuels into electricity, which is an efficient, safe, and environmental-friendly energy conversion technique^[1]. The essence of a solid oxide electrolysis cell (SOEC) is employing SOFC in a regenerative mode to achieve the electrolysis of high-temperature steam to produce hydrogen^[2]. If the power and thermal energy required by electrolysis are supplied by renewable energy or advanced nuclear power, the hydrogen can be produced by a clean, energy-saving, and efficient method, meeting the requirements for sustainable development^[3]. The research of Fujiwara^[4] showed that when SOEC is coupled with the advanced nuclear energy at 800 °C, the hydrogen conversion efficiency of more than 53% can be achieved.

Solid oxide cells (SOCs) can be simultaneously operated in both SOFC and SOEC modes to convert chemical energy of the fuel into power for use and to convert power into fuel for storage when there is a surplus power. SOC is one of the most attractive topics in the field of new energy technologies^[5].

Symmetric SOC (SSOC) with cathodes and anodes made of the same material simplifies the manufacture of SOC^[6]. Compared with traditional SOC, SSOC processing has simpler sintering steps, lower production costs, and better stability in thermal circulation and in redox cycling performance^[7].

The symmetrical electrode is commonly used as both the cathode and anode of SOC. Electrode materials should be stable in structure and chemical performance during oxidation and redox reactions, and have a high conductivity and electrocatalytic activity for both oxygen and fuel gas^[8]. LaCrO₃-based perovskites were firstly applied for symmetrical electrode materials^[9]. These materials have stable performance within a wide partial pressure of oxygen, but their electrocatalytic activity in oxygen and reducing atmospheres is low. Subsequently, more symmetrical electrodes with SOFC perovskite structures have been developed, such as $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$ ^[10], $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.9}\text{Sc}_{0.1}\text{O}_{3-\delta}$ ^[11], $\text{Sm}_{0.7}\text{Sr}_{0.2}\text{Fe}_{0.8}\text{-Ti}_{0.15}\text{Ru}_{0.05}\text{O}_{3-\delta}$ ^[12], and $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$ ^[13]. Their electrocatalytic activity has been improved gradually compared with that of

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the initial symmetrical electrode materials. However, their stability in oxygen and reducing atmosphere is not sufficient for production. Recently, electrode-electrolyte compound symmetrical electrodes have attracted attention because the addition of electrolyte materials can greatly improve the ionic conductivity and stability of the compound electrode^[14,15]. In the preliminary phase, a new redox reversible $\text{La}_{0.4}\text{Sr}_{0.6}\text{Co}_{0.7}\text{Fe}_{0.2}\text{Nb}_{0.1}\text{O}_{3-\delta}$ (LSCFN) symmetrical electrode was prepared in this research. The $(\text{La}, \text{Sr})(\text{Co}, \text{Fe})\text{O}_{3-\delta}$ -based electrode and $\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_{2-\delta}$ (GDC) electrolyte can be mixed according to the mass ratio of 1:1 for obtaining the LSCFN-GDC electrode materials of compound ionic-electronic conduction^[14].

Since more and more energy and environment problems appear, SOC technique shows a broad prospect for its application. In this research, $\text{La}_{0.4}\text{Sr}_{0.6}\text{Co}_{0.7}\text{Fe}_{0.2}\text{Nb}_{0.1}\text{O}_{3-\delta}$ - $\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_{2-\delta}$ as the symmetrical electrodes was prepared and applied in both SOFC and SOEC mode for testing.

1 Experiment

All reagents were of analytical grade and used without further purification. LSCFN-GDC composite electrode powders were prepared by a one-step sol-gel method. $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{C}_{10}\text{H}_5\text{NbO}_{20}$, $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were used as precursors. All metal ion sources were dissolved in deionized water. Then, the citric acid and ethylenediamine tetraacetic acid (EDTA) were added. Aqueous ammonia was added to adjust the pH value, and the solution was stirred at 80 °C until the gel was formed. The gel was then dried in an oven at 90 °C for 12 h to form a gelatinous precursor. Finally, the precursor was calcined in a muffle furnace at 1000 °C for 3 h to obtain the LSCFN-GDC ion-electrode-mixed conductivity electrode powders.

The $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ (LSGM) electrolyte support was prepared via the tape-casting method^[16]. The LSCFN-GDC powders were screen-printed on both sides of the LSGM electrolyte by adding binder (Huatsing Power, China) of the same quality and 20wt% spherical graphite (Huatsing Power, China) of 5 μm in diameter. The symmetric electrodes were sintered at 1000 °C for 5 h. The overall cell structure was LSCFN-GDC||LSGM||LSCFN-GDC.

The microstructure of the cell was observed by scanning electron microscopy (SEM, Merlin). The electrochemical performance and durability of the cells were tested using an in-house constructed testing apparatus. For all tests, the cells were mounted and sealed in an alumina housing. The current density (I)-voltage (V)-power density (P) performance of the cells was tested using the electrochemical workstation (PGSTAT302N Methohm Autolab).

2 Results and Discussion

Fig. 1 shows the X-ray diffraction (XRD) patterns of the LSCFN-GDC symmetrical electrode powder obtained by the one-step calcination method. The corresponding peaks of fluorite and perovskite structures can be distinctly detected in

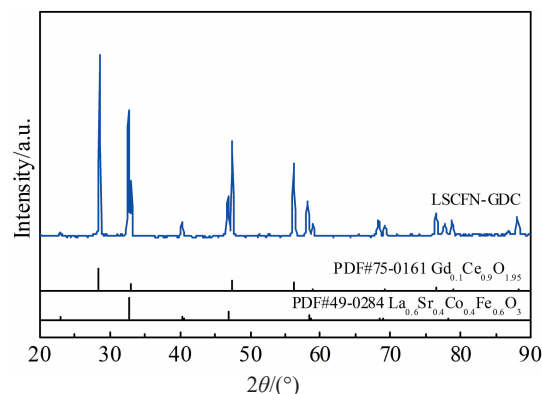


Fig.1 XRD patterns of LSCFN, GDC, and co-synthesized LSCFN-GDC powders

the co-synthesized LSCFN-GDC specimen without any other peaks of impurity phase. The results show that LSCFN and GDC phases are formed after calcination at 1000 °C. LSCFN and GDC retain an independent phase structure without secondary products, which is consistent with the research that $(\text{La}, \text{Sr})(\text{Co}, \text{Fe})\text{O}_{3-\delta}$ -based electrode power and GDC electrolyte power are chemically compatible^[14].

Fig. 2a shows SEM image of cross-section of the symmetrical cell of LSCFN-GDC||LSGM||LSCFN-GDC SSOC. The cell of three-layer structure with the thickness of approximate 150 μm is well sintered, presenting a dense electrolyte and no porosity, which is beneficial for ion conduction and gas isolation. The thicknesses of the anode and cathode are similar at approximate 25 μm. The porous LSCFN-GDC electrode has good contact with the dense LSGM electrolyte, showing no stripping or warpage, which is

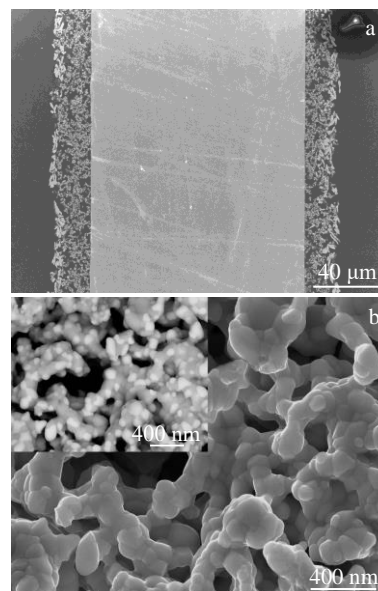


Fig.2 SEM images of cross-section of SSOC (a) and surface of LSCFN-GDC electrode (b)

beneficial for reducing the interface contact resistance. It has a loose porous structure, thus providing channels for the gas diffusion in the electrode.

Fig. 2b shows SEM image of the surface of LSCFN-GDC symmetrical electrode synthesized by one-step method, which was taken in InLends mode. The inset in Fig. 2b was taken in AsB mode, which can clearly distinguish the morphology, particle size, and distribution of LSCFN and GDC particles. As shown in Fig. 2b, LSCFN-GDC electrode has nanoscale GDC particles which appear in white on the dark LSCFN structure. The electrode has a loose and porous structure with surface pores, which is conducive to the transmission of gas in the electrode. The mixture of LSCFN and GDC particles shows an extremely uniform morphology during calcination after one-step preparation method. There is no evidence of particle agglomeration which easily occurs during mechanical mixing. The powder particles prepared by one-step method are small, which increases the three-phase interface area of the reaction and facilitates the catalytic reaction of oxygen and fuel gas on the electrode.

Fig. 3a shows the $V-I$ and $P-I$ curves of LSCFN-GDC||LSGM||LSCFN-GDC SSOC under the fuel atmosphere of H_2 (3% H_2O), H_2 (0.01% H_2S), CH_4 , and C_3H_8 with a flow rate of 50 mL/min and exposure of cathode under the same atmosphere. The maximum power density of the cell is 1.036 W/cm^2 under H_2 (3% H_2O) atmosphere. Using H_2 (0.01% H_2S) as the fuel gas, the power density is 0.996 W/cm^2 , and the cell exhibits good performance. The maximum power density of the single cell with pure CH_4 as fuel gas is 0.479 W/cm^2 . The open circuit voltage (OCV) at corresponding temperature is 1.059 V. The power density of the cell using LSCFN-GDC as the symmetric electrode is approximately 30% higher than that of the LSCFN||LSGM||LSCFN symmetric cell, which indicates that the one-step synthesis method leads to better performance of cell^[16,17]. When the fuel gas changes to C_3H_8 , the power density at 850 °C is 0.952 W/cm^2 , which is almost equal to the power density of the cell in a hydrogen atmosphere.

The electrochemical performance of SSOC was tested at 850, 800, and 750 °C with H_2 (50% H_2O) at the hydrogen

electrode side. The flow rate at the hydrogen electrode was 50 mL/min, and the air was flowed with flow rate of 15 mL/min at the oxygen electrode side. Fig. 3b shows the related $V-I$ curves. When the electrolytic voltage is 1.3 V, the current density of the cell is 0.929, 0.779, and 0.607 A/cm^2 at 850, 800, and 750 °C, respectively. At the same voltage, the current density is increased with increasing the temperature, and the hydrogen production is also increased.

Currently, one of the most serious problems of carbon-based fuel of SOFC anode materials is the performance degradation caused by carbon deposition which may lead to the poor stability of single cell. Similarly, sulfur compounds can poison the anode and reduce the catalytic activity of the anode, resulting in a decline in the performance of the single cell. However, the fuels produced by natural mining and industrial production contain sulfur compounds which are difficult to remove. Therefore, the sulfur resistance of anode materials is also crucial. LSCFN has good redox reversibility in hydrogen. If LSCFN also has redox reversibility in carbon-based fuel atmosphere, it can greatly increase the anti-carbon deposition performance of the cell. To study the coking resistance, sulfur tolerance, and redox reversibility of LSCFN-GDC||LSGM||LSCFN-GDC SSOC, a single cell was discharged at a constant current of 0.4 A/cm^2 . The variation in voltage with time was recorded under the fuel atmosphere of H_2 (0.01% H_2S), CH_4 , and humidified H_2 , and the charging/discharging cycle stability of cell under atmosphere of humidified CH_4 and humidified H_2 was tested.

Fig. 4a and 4b show the long-term stability of the symmetric cell at a constant current of 0.4 A/cm^2 under fuel atmosphere of H_2 (0.01% H_2S) or CH_4 with flow rate of 50 mL/min. The cathode side was exposed to the atmosphere. Firstly, the constant current stability of H_2 (0.01% H_2S) at 750 °C was studied. The initial voltage is 0.816 V. After 100 h of discharge, the voltage is stable. The results show that the LSCFN-GDC composite electrode has good sulfur resistance. Then, at 850 °C, a constant current discharge test was conducted with fuel gas of CH_4 for 500 h. The voltage of the symmetrical cell is stable, which indicates that the electrode prepared by the one-step method also has good carbon

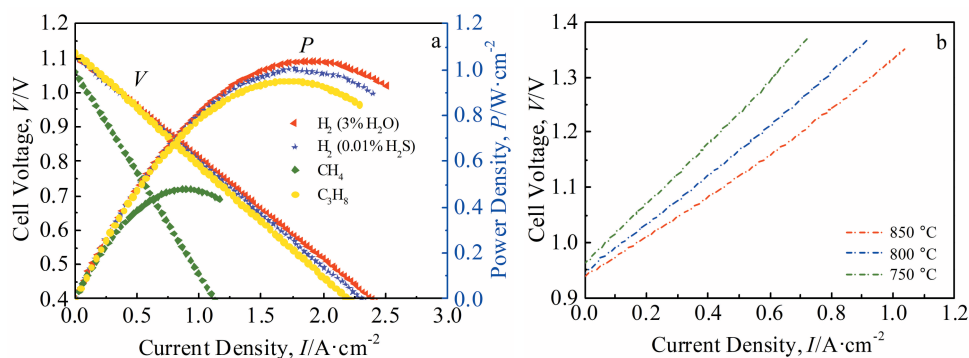


Fig. 3 $V-I$ and $P-I$ curves of SSOC at 850 °C under different fuel atmosphere (a); $V-I$ curves of SOEC mode at different temperatures under H_2 (50% H_2O) atmosphere

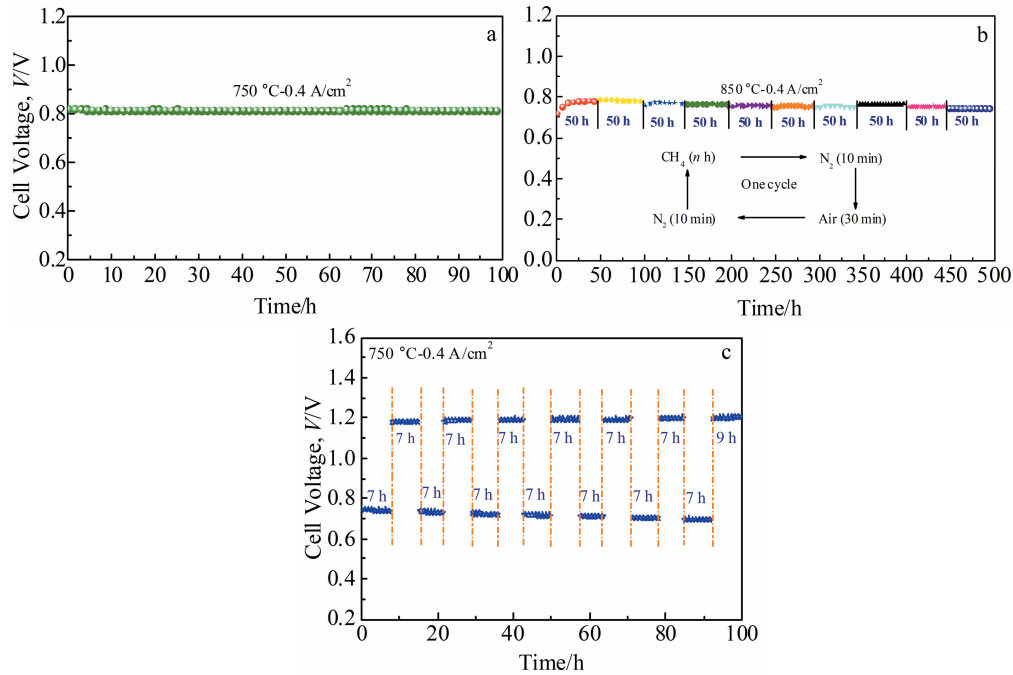


Fig.4 Cell voltage of SSOC at constant current load of 0.4 A/cm^2 under different atmosphere: (a) H_2 (0.01% H_2S) at $750 \text{ }^\circ\text{C}$, (b) CH_4 at $850 \text{ }^\circ\text{C}$, and (c) SOFC/SOEC mode at $750 \text{ }^\circ\text{C}$

deposition resistance. In addition, the redox cycling test was simultaneously conducted at the anode every 50 h for 10 cycles. As shown in Fig. 4b, the symmetrical electrode of LSCFN-GDC prepared by the one-step method shows good carbon storage resistance and excellent redox cycle reversibility under humidified CH_4 atmosphere. In brief, LSCFN-GDC electrode has excellent stability against sulfur and carbon deposition, and can be applied under long-term oxidation-reduction conditions.

Fig.4c shows the charging/discharging cycle stability of the LSCFN-GDC||LSGM||LSCFN-GDC cell under the constant current condition of 0.4 A/cm^2 at $750 \text{ }^\circ\text{C}$, and the testing atmosphere at anode (hydrogen) and cathode (oxygen) electrodes is the same as that of SSOC. Each cycle is about 7 h of charging and 7 h of discharging, and the total time of all cycles is approximate 100 h. As shown in Fig. 4c, after 7 cycles, the discharge voltage drops from the initial voltage of 0.77 V to 0.74 V. The decay ratio of the cell in SOFC discharging mode is approximate 3.9%, while the charging voltage in the charging mode has a small and stable decay ratio.

3 Conclusions

1) A $\text{La}_{0.4}\text{Sr}_{0.6}\text{Co}_{0.7}\text{Fe}_{0.2}\text{Nb}_{0.1}\text{O}_{3-\delta}\text{-Gd}_{0.2}\text{Ce}_{0.8}\text{O}_{2-\delta}$ (LSCFN-GDC) symmetrical electrode is prepared by a one-step synthesis method, and the LSCFN-GDC|| $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.83}\text{Mg}_{0.17}\text{O}_{3-\delta}$ (LSGM)||LSCFN-GDC single cell is constructed using LSGM as the electrolyte. The maximum power densities of the cell are 1.036, 0.996, 0.479, and 0.952 W/cm^2 at $850 \text{ }^\circ\text{C}$ under atmosphere of H_2 (3% H_2O), H_2 (0.01% H_2S), CH_4 , and C_3H_8 , respectively. The current density at the electrolytic voltage of

1.3 V is 0.943 A/cm^2 during the electrolysis of H_2 (50% H_2O).

2) The cells have good coking-resistance, sulfur-tolerance, and redox cycle stability. It shows small performance degradation after discharging at a constant current of 0.4 A/cm^2 for 100 and 500 h under H_2 (0.01% H_2S) and CH_4 atmosphere, respectively. LSCFN-GDC electrode has excellent stability against sulfur and carbon deposition and can be applied under long-term oxidation-reduction conditions.

3) LSCFN-GDC electrode synthesized by one-step method has good catalytic performance and shows excellent stability under hydrogen and carbon-based fuel atmosphere. This research shows the application potential of LSCFN-GDC for the development of symmetric solid oxide cell (SSOC) in the field of sustainable energy process.

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$\text{La}_{0.4}\text{Sr}_{0.6}\text{Co}_{0.7}\text{Fe}_{0.2}\text{Nb}_{0.1}\text{O}_{3-\delta}$ - $\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_{2-\delta}$ 应用于可逆固体氧化物电池对称电极

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摘要: 为制备一种高催化性的对称型固体氧化物电池电极, 采用一步法合成了 $\text{La}_{0.4}\text{Sr}_{0.6}\text{Co}_{0.7}\text{Fe}_{0.2}\text{Nb}_{0.1}\text{O}_{3-\delta}$ - $\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_{2-\delta}$ (LSCFN-GDC)。以 LSCFN-GDC 为电池阳极和阴极, $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.83}\text{Mg}_{0.17}\text{O}_{3-\delta}$ (LSGM) 为电解质, 采用流延和丝网印刷工艺制备了结构为 LSCFN-GDC||LSGM||LSCFN-GDC 的电解质支撑型固体氧化物电池。分别采用固体氧化物燃料电池 (SOFC) 及固体氧化物电解池 (SOEC) 2 种模式对对称电池性能进行了测试。在 850 °C 测试温度下, 分别采用湿 H_2 (3% H_2O)、 H_2 (0.01% H_2S)、 CH_4 和 C_3H_8 为燃料气, 电池最大功率密度分别为 1.036、0.996、0.479 和 0.952 W/cm^2 , 电解 H_2 (50% H_2O) 时, 1.3 V 电解电压下电池电流密度为 0.943 A/cm^2 。LSCFN-GDC 具有良好的耐积碳、抗硫和氧化还原稳定性能, 能够在湿 H_2 (0.01% H_2S)、 CH_4 、 H_2 (3% H_2O) 及 H_2 (50% H_2O) 环境中稳定运行 700 h。实验结果表明, 一步合成法是一种简便而优化的电极制备方法, LSCFN-GDC||LSGM||LSCFN-GDC 固体氧化物电池 (SOC) 具有广阔的应用前景。

关键词: LSCFN-GDC 对称电极; 可逆固体氧化物电池; 耐积碳; 抗硫

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