



Article Enhanced Electrolysis of CO₂ with Metal–Oxide Interfaces in Perovskite Cathode in Solid Oxide Electrolysis Cell

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Abstract: The application of solid oxide electrolysis cell in CO_2 electroreduction is a hot research topic at present, but the development of low–cost catalysts with high catalytic activity has always been a challenge for this work. Herein, we use NiCu alloy nanoparticles to modify the perovskite LSCM electrode to build a metal–oxide active interface to obtain high catalytic performance. At 850 °C, 4.66 mL min⁻¹ cm⁻² CO productivity and 97.7% Faraday current efficiency were obtained. In addition, the current remained stable during the 100 h long–term test, indicating that the active interface has the dual effect of improving catalytic performance and maintaining cell durability.

Keywords: active interface; SOEC; CO2 electrolysis



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1. Introduction

Nowadays, the problems of environment and energy in the world have become increasingly prominent, and the use of fossil fuels has directly led to a large area of environmental pollution [1–3]. With the burning of fossil fuels, the concentration of CO_2 in the atmosphere is increasing, resulting in serious environmental pollution problems, such as haze, acid rain and global warming [4–6]. Therefore, converting CO_2 into economically valuable fuel can not only alleviate the global warming caused by greenhouse gas emissions, but also is the inevitable choice of the development of the times [7–9].

Electroreduction and conversion of CO₂ is an effective way to realize CO₂ recovery and reuse. The common methods for CO_2 electroreduction are H-type cells, but they are susceptible to CO₂ mass transport limitations and cannot achieve high product generation rates. As the limitation of CO_2 gas transmission can be eliminated, flow cells are also widely used. Polymer electrolyte membrane (PEM) flow cells are the most promising device for CO_2 reduction in practice, which are usually assembled from a cathode and anode current collector, cathode and anode flow plate and membrane electrode assembly (MEA). However, the lack of reference electrodes and the strong corrosion caused by high overpotentials can make potential measurements difficult. The microfluidic flow cells (MFC) can be used to evaluate the performance of catalysts for the electroreduction of CO_2 under different operating conditions, but the structure is too sensitive to stresses caused by the transmembrane to be applied on a large scale [10-13]. Solid oxide electrolysis cells (SOEC) act as a kind of energy conversion device, which can convert electrical energy into chemical energy, so it greatly improves the energy efficiency. Compared with other electrolysis processes, CO₂ electrolysis in a solid oxide electrolysis cell also has the advantages of carbon deposition resistance, all-solid-state design, and the use of non-precious metal catalysts [14–16].

At present, the conversion efficiency of CO_2 is still limited by the low activity of the electrode catalyst. For this reason, researchers improve the catalytic activity by doping

precious metals (such as Ru and Au) [17,18]. However, although the catalytic efficiency has been improved, it faces high costs. The non-noble metals are not only easy to obtain and cheap, but also easy to be exsolved to form active nanoparticles under the reducing atmosphere, which is the preferred choice of catalysts. $La_{0.7}Sr_{0.3}Cr_{0.5}Mn_{0.5}(NiCu)_xO_{3-\delta}$ $(LSCrM(NC)_x)$ is one of the commonly used cathode materials in SOEC because of its excellent electronic and ionic conductivity as well as high redox stability [19,20]. Zhang et al. proved that the electrolysis of LSCrM electrode in symmetrical cells has good current activation performance [21,22], with the electrolysis efficiency of CO₂ reached 69%, 58% and 56% at 800 °C, at 1.0 V, 1.5 V and 2.0 V, respectively. Due to the poor catalytic activity of the traditional LSCrM cathode, its performance for electrocatalytic CO₂ reduction is limited. In recent years, scientists have found that the doping of non-precious metal oxide significantly improves the electrochemical performance of LSCrM cathodes [23]. The exsolution of Ni nanoparticles from the catalyst has been proved to be an effective way to improve the catalytic activity of CO_2 electrolysis [24]. However, the long-term instability of nanoparticles remains a major challenge because the agglomeration of nanoparticles at high temperatures leads to a decline in catalytic performance. According to recent studies, Cu nanoparticles have excellent CO_2 adsorption properties and anti-coking properties [25]. Therefore, in order to improve the catalytic performance of LSCrM electrode, we designed an effective method to improve the performance of porous electrodes by immobilizing NiCu alloy catalytic active nanoparticles on the surface of the porous electrode. This alloy catalyst makes use of the interaction between nickel and copper to greatly improve the catalytic activity and anti-coking performance of LSCrM cathode materials in the electrolytic reaction of CO₂.

In this work, we synthesize a range of LSCrM(NC)_x, doped excessive NiCu at the B position, and made NiCu exsolve from the lattice of LSCrM through reduction pretreatment to form active metal alloy nanoparticles, thus promoting the electrochemical conversion of CO_2 .

2. Results and Discussion

The general chemical formula of perovskite oxide is ABO₃, in which a rare earth or alkaline earth metal element is at position A, and a transition metal element is at position B. Excellent ion electron mixed conductor properties can be obtained by doping. The transition at position B is easy to be exsolved under reducing atmosphere, and different transition metals are easy to form alloys [26,27]. A series of LSCrM(NC)_x electrode materials were analyzed by XRD; the diffraction pattern is as shown in Figure 1a,b. Figure 1a is the XRD spectrum of LSCrM(NC)_x synthesized in liquid phase, which displays a pure perovskite phase without other impurity peaks, indicating that excess metal Ni and Cu at the B site have successfully entered the lattice of LSCrM. The spectrogram of oxidized LSCrM(NC)_x powder after reduction by 5% H₂/Ar is shown in Figure 1b. Compared with Figure 1a, there is a new peak at 44.2° [14,28], which is confirmed to be NiCu alloy, illustrating that the NiCu at B site is exsolved from the lattice of LSCrM under the reducing atmosphere. In addition, except for the NiCu alloy peak, the phase of LSCrM remains unchanged after high-temperature reduction, exhibiting its excellent structural stability.

The XPS spectrum of NiCu for a proper amount of freshly fired LSCrM(NC)_x liquid powder and a powder with 5% H₂/Ar reduction is as shown in Figure 2. The doped Ni and Cu under oxidation state exist on LSCrM substrate in the form of 2+, as shown in Figure 2a,b, respectively. The two main peaks Ni²⁺ 2p3/2 and Ni²⁺ 2p1/2 are accompanied by two satellite peaks, as is Cu. After reduction, the binding energies of the peak positions of Ni and Cu are reduced, and coexistence of Ni⁰ and Cu⁰ is observed [29,30], indicating that NiCu alloy exists in the LSCrM(NC)_x sample, which is in agreement with the results of previous XRD tests. These valence state changes caused by reduction treatment will theoretically lead to lattice distortion, thus promoting ion transport.



Figure 1. XRD characterization of LSCrM(NC)_x samples. (a) Unreduced and (b) reduced samples.



Figure 2. The chemical valence state of the elements. (**a**) Ni 2p and (**b**) Cu 2p XPS of unreduced LSCrM(NC)_x; (**c**) Ni 2p and (**d**) Cu 2p XPS of reduced LSCrM(NC)_x.

Figure 3a reveals the scanning electron microscope view of cross–section for a complete single cell. The dense LSGM electrolyte is conductive to the transmission of electrons and can isolate the reaction gas of the cathode and anode. The volatilization of organic matter at high temperature causes the porous structure of the electrode, which not only promotes the diffusion of reaction gas, but also ensures full contact between CO₂ and catalyst [31]. Thermogravimetric analysis of LSCrM(NC)_x electrode material in a reducing atmosphere (5% H₂/Ar) is shown in Figure 3b. The sharp drop in weight within 100 °C is due to the evaporation of water in the material. The slow weight reduction in the second stage is owing to the continuous escape of lattice oxygen in the material, leaving oxygen vacancies that cause weight reduction. Among them, the weight loss of LSCrM(NC)_x is also affected by the alloy formed by the exsolution of doped NiCu from the lattice [32]. To further observe the metal nanoparticles, we take pictures of the microstructure of catalytic materials with different doping levels after reduction, as shown in Figure 3a,b. Metal alloy



nanoparticles with average particle size less than 50 nm are evenly distributed, and the amount is positively correlated with the doping amount.

Figure 3. Microscopic morphology and thermogravimetry. (a) SEM images of cell cross–sections, (b) the TGA of LSCrM(NC)_x at 5% H₂/Ar, SEM of reduced (c) LSCrM(NC)_{0.025} and (d) LSCrM(NC)_{0.075}.

More evidence to prove the exsolution of NiCu alloy is shown in Figure 4a,b by HRTEM. Careful observation finds that the lattice stripes of the particles and the substrate are different, indicating that NiCu nanoparticles are exsolved from the substrate. NiCu alloy nanoparticles are anchored on the LSCrM skeleton, demonstrating that there is a strong interaction between metal particles and the interface. Figure 4b represents that the lattice stripes of NiCu alloy nanoparticles have a lattice spacing of 0.178 nm, corresponding to the (200) face of NiCu alloy. Furthermore, the atomic proportions of elements in the sample are analyzed by EDS, as shown in Figure 4c. In the table inserted in Figure 4c, except for the copper atom, the atomic proportion of other elements is basically consistent with the chemical formula and doping amount, while the large proportion of Cu atoms is attributed to the sample preparation on the copper mesh.



Figure 4. HRTEM with element dispersive X-ray spectroscopy analysis. (a) HRTEM image of reduced LSCrM(NC)_x and lattice spacing micro-image of the exsolved (b) NiCu alloy, and (c) EDS analysis of the corresponding regions.

The single cell after reduction pretreatment starts to test its electrochemical performance and catalytic performance. Figure 5a manifests the instantaneous current density of the cell at 0.6–1.6 V, the increases of voltage play a positive role in the enhancement of current density. On the one hand, the increase of voltage strengthens the electric field of the conductor, and on the other hand, the active interface formed by the exsolved alloy particles and the oxide substrate contributes to the directional migration of electrons [33]. Figure 5b is the current density of the cell running for 10 min under different voltages. The current density of the electrode LSCrM(NC)_{0.075} doped with NiCu is stable at 0.68 A cm⁻² at 1.6 V, which is much higher than that of the pure LSCM 0.31 A cm⁻². In general, the electrochemical performance of the electrode loaded with metal nanoparticles is better than that of the electrode without metal nanoparticles, as well as the CO₂ conversion performance, see Figure 5c,d for details. $LSCrM(NC)_{0.075}$ -SDC electrode used for CO₂ electrolysis has the best catalytic effect in this series of materials, with the production of CO reaching 4.66 mL min⁻¹ cm⁻², and the current efficiency up to 97.7%, which is much higher than that of pure phase LSCrM-SDC electrode. Under the same conditions, the trends of current density, CO productivity and current efficiency are consistent. These results prove that NiCu alloy nanoparticles, as the active site of the reaction, can promote the electroreduction of CO₂. However, too much doping will be counterproductive, for example, the performance of $LSCrM(NC)_{0,1}$ -SDC electrode will be degraded due to the inevitable agglomeration of alloy nanoparticles. Table 1 shows the electrochemical performance of relevant literatures with different metal doping, mainly including the single metal element and its multiple element co-doping.



Figure 5. Performance diagram of LSCrM(NC)_x-SDC. (a) Transient current, (b) short-term current, (c) CO yield from electrolytic CO₂ at different voltages and (d) corresponding Faraday current efficiency.

Table 1. The summary of electrochemical performance of the perovskite cathode doped with different metal elements.

Dopant	Electrolyte	Working Conditions	Current Density	Reference
NiCu	LSGM	850 °C, 1.6 V	$0.68 \mathrm{A} \mathrm{cm}^{-2}$	This work
$Ce_{0.9}Mn_{0.1}O_{2-\delta}$	YSZ	800 °C, 1.8 V	$0.52 \mathrm{~A~cm^{-2}}$	[23]
Ca	SSZ	800 °C, 1.2 V	$0.27 \mathrm{~A~cm^{-2}}$	[34]
Cu	LSGM	750 °C, 1.65 V	1.82 A cm^{-2}	[35]
Ni	YSZ	800 °C, 2 V	$0.33 \ {\rm A} \ {\rm cm}^{-2}$	[36]
CaFe	SSZ	800 °C, 1.6 V	$0.6 \ {\rm A} \ {\rm cm}^{-2}$	[37]

Figure 6a–e reveal the in situ AC impedance spectra of each electrode material at a specific voltage, which are often used to analyze the reasons for the improvement of cell performance [38]. With the increase of voltage, the impedance shows a negative correlation, because the increase of voltage can accelerate the transfer of electrons. The total polarization resistance of each electrode is shown in Figure 6e, the LSCrM(NC)_{0.075}–SDC electrode again emerges with excellent performance, with the lowest impedance value of 0.51 Ω cm². This result attests that the reduction of electrode polarization resistance is closely related to the effect of alloy nanoparticles.



Figure 6. Impedance spectra of LSCrM(NC)_x at different voltages. (a) LSCrM, (b) LSCrM(NC)_{0.025}, (c) LSCrM(NC)_{0.05}, (d) LSCrM(NC)_{0.075}, (e) LSCrM(NC)_{0.01}, and (f) the corresponding polarised resistance of LSCrM(NC)_x.

Long-term tests with CO₂ electrolysed by reduction pretreated LSCrM(NC)_{0.075}–SDC is shown in Figure 7a. The current density is stable at 0.33 A cm⁻² at 850 °C and 1.2 V even at 100 h without decay, indicating this exsolved cathode material has excellent long-term stability. Figure 7b shows a micrograph of the cell after 100 h of CO₂ electrolysis. We can clearly see that the NiCu alloy nanoparticles are still attached to the almost unchanged porous electrode surface, suggesting that the metal oxide interface formed by the combination of the exsolved NiCu alloy nanoparticles and the structurally stable LSCrM substrate is the key to maintaining superior performance.



Figure 7. Long–term tests and morphology. (**a**) Long–term performance of electrolysis of CO₂ 100 h and (**b**) micrographs after electrolysis.

3. Experimental

The perovskite LSCrM(NC)_x powders are synthesized by the glycine–nitrate method [39,40]. Appropriate amounts of lanthanum nitrate, strontium nitrate, chromium nitrate, manganese nitrate, nickel nitrate, copper nitrate and glycine were weighed and dissolved in ultrapure water according to the stoichiometric ratio. Then they were heated at 200 °C until evaporation and combustion. The resulting powder was placed in a muffle furnace, heated at a rate of 3 °C per minute and held at 1300 °C for 6 h. Ce_{0.8}Sm_{0.2}O_{3- δ}(SDC) powders are synthesized though a glycine–nitrate combustion method with appropriate amounts of Ce(NO₃)₃·6H₂O and Sm₂O₃ followed by 800 °C for 3 h in air. La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O₃ (LSGM) powder is prepared by a solid–state reaction, by mixing appropriate amounts of the corresponding oxides and heating to 1300 °C in a muffle furnace and holding for 6 h. The resulting sample was weighed 0.65 g and pressed into a 2 cm diameter disc, then heated to 1450 °C in the furnace and held for 10 h to obtain a dense electrolyte carrier.

The appropriate amount of LSCrM and SDC powder is added to the paste consisting of α -pinoresinol, tapioca starch and ethyl cellulose in the ratio of 65:35 by mass. Then they are mixed and ground for 2 h. The obtained samples are coated on both sides of the LSGM surface and heated at 1000 °C for 3 h to form cell pellets. Finally, the silver wire is fixed to both sides of the cell pellet by silver paste and then maintained in the furnace at 550 °C for half an hour, and the resulting sample is the LSCrM–SDC cell. The cell consists of about 1 mm electrolyte and about 40 µm porous anode and cathode, among them, the active area of the electrode is about 0.5 cm⁻², which is an important data for the later calculation of impedance density and current density. Before testing, the LSCrM–SDC cell is pretreated by reduction with 5% H₂/Ar in a tube furnace and then electrochemically measured by CO₂ electrolysis at 850 °C. The reaction gas CO₂ of cathode is cracked into CO and O^{2−} under the action of high temperature and applied voltage, while the O^{2−} is transmitted to the anode through a dense electrolyte to form oxygen. The specific reaction procedure is as follows: CO₂ + 2e⁻→CO + O^{2−} (cathode), O^{2−} −2e⁻→1/2O₂ (anode).

X–ray powder diffraction (XRD, Cu–K α , Miniflex600, Rigaku, Tokyo, Japan) is used to characterized the phase of the generated material (LSCrM(NiCu)_x). X–ray photoelectron spectroscopy (XPS, AlKa, ESCALAB 250Xi, Waltham, MA, USA) is used to characterize the changes in valence and bonding of samples. High–resolution transmission electron microscopy (HRTEM, Tecnai F20, Hillsboro, OR, USA) and a scanning electron microscope (SEM, SU–8010, Tokyo, Japan) are used to characterize the microstructure of the electrodes samples and the composition of the electrode material is analyzed by energy dispersive X–ray spectrometer (EDS) of SEM. The relevant electrical performance tests are recorded by an electrochemical workstation (IM6, Zahner, Kansas, MO, USA). The yield of carbon monoxide produced by electrolysis of CO₂ is analyzed by gas chromatography (GC–2014, Shimadzu, Kyoto, Japan).

4. Conclusions

In conclusion, by doping at the B position, alloy metal nanoparticles are exsolved from the oxide substrate to serve as the active site of the reaction, and form an active metal—oxide interface with the substrate to promote the adsorption and decomposition of CO_2 , thus accelerating the CO_2 electrolysis reaction. The electrode with the best doping amount, LSCrM(NC)_{0.075}, has outstanding performance, including 4.66 mL min⁻¹ cm⁻² CO yield and 100 h of long—term stable operation. The results suggest that the application of interface engineering in SOEC has a good prospect.

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