



Efficient Carbon Dioxide Electrolysis Based on Perovskite Cathode Enhanced with Nickel Nanocatalyst



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ABSTRACT

The Mn-doped titanate can lead to the remarkable chemical adsorption of CO₂ uncovering the tremendous potential for direct high temperature CO₂ electrolysis. Unfortunately, the application of this material is still limited by insufficient carbon dioxide splitting and electrocatalytic activity. This study reports the improved electrocatalytic activity and Faraday efficiency of composite cathode with exsolution of nickel nanocrystals on the surface of doped titanate for CO₂ electrolysis. The electrical conductivity has been enhanced in the presence of metallic Ni in contrast to bare Mn doped titanate and further correlated to the electrochemical performance of the composite cathodes. Promising electrode polarization has been demonstrated based on the titanate with nickel nanoparticles and the Faraday efficiency is improved for the direct CO₂ electrolysis at high temperatures.

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1. Introduction

Solid oxide electrolyzer (SOE) has attracted a great deal of interest and is widely considered as a promising electrochemical device for renewable energy with high conversion efficiency for the future [1–5]. Carbon dioxide electrolysis is able to produce clean fuel using external electricity owing to its favorable kinetics and thermodynamics at high temperature in a SOE [6,7]. The composite cathode based on conventional Ni-YSZ cermet of excellent catalytic properties displays excellent performance for the electrolysis of steam or carbon dioxide [8–14]. However, it requires a proper concentration of reducing gas to avoid the oxidation of metallic Ni which in turn would cause a loss of electrical conductivity and even failure of the cathodes [3].

Perovskite titanate and chromate (La_xSr_{1-x}TiO_{3-δ}, LSTO; La_xSr_{1-x}Cr_yMn_{1-y}O_{3-δ}, LSCM) have been proved to have stable structure and reasonable conductivity in reducing atmosphere within a broad temperature region [14,15]. So far, a great deal of effort has been made to the research of titanate as a promising anode for solid oxide fuel cell [16–22]. Titanate and chromate have been utilized for the hydrogen electrodes of solid oxide electrolyzers which show good polarization resistance [14,23]. On the other

hand, the perovskite LSTO would be a good fit for the strong reducing atmosphere and result in promising polarization performance that occurs in the cathodes of solid oxide electrolyzers. The LSTO cathodes have been also reported to be very stable in an atmosphere with high concentration of steam or carbon dioxide in a solid oxide electrolyzer. This is due to that the perovskite structure can be retained upon heat treatment in air and pure hydrogen even at high temperature. Solid oxide electrolyzer shows good performance for electrolysis of CO₂/CO system with high efficiencies and keeping the CO content at a lower level can decrease the carbon deposition risk in a SOE which indicates the promising direct carbon dioxide electrolysis [24–27]. The Faraday efficiencies about 100% of SOE can be achieved in proper condition designs which show great potential for the steam or carbon dioxide electrolysis [26]. Mn-doped titanate has been studied with excellent performance for polarization and catalytic property [15]. Recently, we have demonstrated that the remarkable chemical-adsorption of CO₂ has been achieved on Mn-doped titanate with the onset temperature of strong desorption to be extended to as high as approximately 800 °C which is the common operation temperature for solid oxide carbon dioxide electrolyzers. The ionic conductivities of the Mn-doped titanate are remarkably enhanced by 1–2 orders of magnitude in contrast to LSTO at intermediate temperatures in reducing or oxidizing atmospheres [28]. Sufficient oxygen vacancies in the perovskite titanate can be created by the active Mn of multi-oxidation states to accommodate

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and activate CO₂ molecules in the forms of strong bonding between the oxide ions in CO₂ and the nearest cations on the (La, Sr)O- or (Ti, Mn)O₂-terminated facets. The CO₂ chemical absorption on the ceramic can benefit the conversion of gas in a cathode of a solid oxide electrolyzer. However, cathode performance for carbon dioxide splitting is still limited by the low catalytic properties of the bare ceramics for cathodes of the solid oxide electrolyzers. On the other hand, the absorption process can be limited due to that CO₂ may leave the surface readily which also leads to the difficult conversion process, therefore, it is important of the catalytic property for the CO₂ conversion, especially in the limited absorption process, besides, the exsolution of metal nanoparticles provide a promising way to high efficient electrolysis of carbon dioxide.

So far, a great deal of efforts have been devoted to the study of Ni, Fe, Pt and Pd commonly utilized as the excellent catalysts for biogas reforming, water gas shift reaction and catalytic conversion of CO₂ at low or high temperatures [29–36]. Nanostructured barium oxide/nickel (BaO/Ni) has been reported to facilitate carbon removal reactions with the nanostructured interfaces between oxides and metals which readily improve chemical reactions [37]. The chemical conversion of dissociated species can perform near the interfaces, then at the triple-phase boundary (TPB) of the electrodes. These nano sized metals are also widely loaded on some oxygen-deficient ceramic substrates including CeO_{2-δ} and Ce_xZr_{1-x}O_{2-δ} in the form of heterogeneous catalysts [38,39]. The nanoparticles can become the electrocatalytic active sites for the water gas shift reaction in a reducing atmosphere with substantially improved performance attributed to the promotion of the nanocatalyst and oxygen deficient substrate [10].

The coupling of nano metal and ceramic substrates significantly enhances the catalytic activity because of the combination of the excellent electrocatalytic active properties of nano-sized catalyst and the efficient accommodation/activation of reactant molecules in the oxygen-deficient sites on the substrate surfaces. However, the agglomeration of the nano metals which is easily formed on the substrate surfaces remains a limitation that degrades the electrocatalytic performance at high temperatures [40].

Recently, *in-situ* growth of nanoparticles from the substrate offers a promising way for the coupling of nanocatalysts and ceramics in control of non-stoichiometry reported by Neagu and Irvine et al. [31]. The exsolution of a proportion of the cations from the B-site is able to form the exsolved metal nanoparticles on the surface of the perovskite ABO₃ structure in the reducing atmosphere at high temperatures, for instance, 800 to 1400 °C. It is partly attributed to that the host lattice tends to keep stable to accommodate the vacancies including introduced or inherent oxygen vacancies. In addition, A-site deficient ceramic has been proved to be beneficial for the metal exsolution and stability between the metal and the substrate [4]. The doped cations at the B-site are chosen according to the cation-size which should be proper for the lattice. *In-situ* growth of nanoparticles from the ceramics achieves the combination of the electrocatalytic property of the nano metal and the redox stability of substrate. Meanwhile, the *in-situ* growth of nanocatalyst can also lead to a stable anchorage for the nanocatalyst on the substrate [31]. The metal nanoparticles grow through a reversible exsolution of the metal dopant *via* a high-temperature treatment in reducing atmosphere to anchor on the surface which is expected to enhance the electrocatalytic kinetics and the high-temperature stability of the metal nanoparticles [4,9]. The nanoparticles can also benefit the good catalytic properties of the composite cathodes for electrolysis of carbon dioxide at high temperatures in a solid oxide electrolyzer.

In this work, the perovskite Mn doped titanate with Ni substituted at the B-site is investigated as cathode materials of

solid oxide electrolyzers. After reduction, electrocatalytic active nickel metal is exsolved to grow on the Mn-doped titanate to form active catalyst while it combines with the oxygen vacancies on the titanate surfaces for absorption and electrochemical conversion of CO₂. The cathode performance based on this composite is then systematically investigated for direct CO₂ electrolysis at 800 °C.

2. Experimental

2.1. Synthesis

All the chemicals used in the current investigation were of analytical grade and purchased from SINOPHARM Chemical Reagent Co., Ltd (China). The (La_{0.2}Sr_{0.8})(Ti_{0.9}Mn_{0.1})O_{3-δ} (LSTM) were synthesized with a solid-state reaction method in which the powders of La₂O₃, SrCO₃, TiO₂ and MnO₂ were mixed together, ball-milled for 15 min, dried, pressed into pellets at 5 Mpa and fired at 1400 °C for 20 h in air [41–44]. Similar synthesis method was employed for (La_{0.2}Sr_{0.8})_{0.9}(Ti_{0.9}Mn_{0.1})_{0.9}Ni_{0.1}O_{3-δ} (LSTMN) powders as stated above. Perovskite La_{0.2}Sr_{0.8}MnO₃ (LSM) was prepared with La(NO₃)₃·6H₂O, Sr(NO₃)₂ and Mn(NO₃)₂·4H₂O dissolved in de-ionized water followed by a heat treatment at 1200 °C for 10 h in air using a combustion method [45–47]. About 2.0 g LSTM or LSTMN powders were pressed into bars and fired in air at 1400 °C for 10 h, which were later reduced in 5%H₂/Ar at 1400 °C for 10 h, and then utilized for conductivity tests with DC 4-point method [48,49]. The relative densities reached approximately 89.3% for LSTM and ~90.6% for LSTMN, respectively. The 1-mm-thick YSZ electrolyte was fabricated with 8 mol% Y₂O₃ stabilized ZrO₂ by dry-pressing the powders into a green disk with diameter of ~20 mm which was sintered at 1550 °C for 20 h in air [50–52].

2.2. Characterization

X-ray diffraction (XRD) (Cu Kα, X'Pert Pro PAN Analytical B.V.) was performed to identify the phase formation. The XRD patterns were refined with the software of General Structure Analysis System (GSAS) with edit back ground of the refinement based on the shifted Chebyshev. At first, the crystal cell is refined, then the peak parameters, the structure and temperature factors are performed in order with the GSAS software [53]. High-resolution transmission electron microscope (HR-TEM) (JEM-2100F, JEOL) and field emission scanning electron microscope (FESEM) (SU8020, HITACHI) were used for charactering the microstructures of the materials and electrodes. As for the chemical state of the ceramics, X-ray photoelectron spectroscopy (XPS) (ESCALAB25, Thermo) was employed for the LSTM and LSTMN powders before and after reduction. A multi-meter (Keithley 2000, Keithley) was utilized for the conductivity tests of the reduced samples in 5%H₂/Ar at 800 °C, while the tests of oxidized samples were carried out in air, meanwhile, an online oxygen sensor (Noveltech Type 1231, Noveltech) was employed for simultaneously recording the oxygen partial pressure (pO₂) controlled by flowing 5%H₂/Ar for enough time until stable.

2.3. Cells fabrication and tests

The cathode/anode slurry was formed with an equal amount of the LSTM/LSM and YSZ powders by 50:50 wt% in ethyl cellulose-terpineol, and then printed onto the two opposite surfaces of YSZ discs to assemble symmetrical cells with the configurations of LSTM-YSZ/YSZ/LSTM-YSZ and LSTMN-YSZ/YSZ/LSTMN-YSZ. The solid oxide electrolyzers with configurations of LSTM-YSZ/YSZ/LSM-YSZ and LSTMN-YSZ/YSZ/LSM-YSZ were prepared in the

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