Enhanced Surface Exchange Activity and Electrode Performance of $(\text{La}_{2-2x}\text{Sr}_{2x})(\text{Ni}_{1-x}\text{Mn}_x)\text{O}_{4+\delta}$ Cathode for Intermediate Temperature Solid Oxide Fuel Cells

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Abstract

Surface exchange kinetics of Ruddlesden-Popper (R-P) phase lanthanum nickelates upon Mn doping as an intermediate temperature solid oxide fuel cells (IT-SOFCs) cathode is investigated for the first time in this communication. To promote the exchange rate in oxygen reduction reaction (ORR) on nickelates, Mn is partially substituted for Ni. The oxygen exchange resistance is accurately measured by electrochemical impedance spectroscopy (EIS) with dense thin layer cathode. It is found that Mn substantially promotes the surface kinetics; a surface exchange coefficient (k) of 1.57×10^{-6} cm/s is obtained at 700°C for $\text{La}_{1.8}\text{Sr}_{0.2}\text{Ni}_{0.9}\text{Mn}_{0.1}\text{O}_{4+\delta}$ (Sr20Mn10), ~80% higher than that of the undoped $\text{La}_2\text{NiO}_{4+\delta}$ (LNO). To our best knowledge, such coefficient is the highest values among the currently available R-P phase IT-SOFC cathodes. The corresponding polarization resistances (R_p) are evaluated on porous electrodes. R_p for LNO is $0.74 \text{ } \Omega\text{cm}^2$ at 750°C, but decreases significantly to $0.42 \text{ } \Omega\text{cm}^2$ for Sr20Mn10 which is remarkably improved compared to the reported values in the literature for $\text{La}_2\text{MO}_{4+\delta}$ materials (M=transition metal). Those promising results demonstrate that Mn-doped LNO is a new excellent cathode material for IT-SOFC.

Keywords: Intermediate temperature solid oxide fuel cell, Ruddlesden-Popper phase, oxygen reduction reaction, surface exchange coefficient

1. Introduction

Solid oxide fuel cells (SOFCs) are recognized as one of the most promising energy conversion systems due to their high efficiency and minimal environment impact [1]. To overcome the key

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limiting issues associated with the high operating temperature (800-1000°C), tremendous effort has been devoted to reducing operation temperature of SOFCs to the intermediate temperature (IT) region (650-800°C) so as to reduce system costs, relax the requirement for interconnects, and mitigate long-term degradation [2-3]. However, concomitant with the lowered temperature is the significant reduction in the electrode activity [4]. In particular, for the state of the art Ni/Y_{0.16}Zr_{0.84}O_{2-δ}(YSZ)/YSZ/(LaSr)MnO_{3±δ}(LSM) fuel cells, the cathode suffers more severely from lowered temperature than the anode, e.g. LSM exhibits polarization resistance of 5~20 Ωcm² at 700°C [5-6]. Therefore, the exploration of novel IT cathode materials with reduced polarization resistance is imperative to minimize the overall energy loss. In recent, A₂BO_{4+δ} R-P phase lanthanum nickelates have attracted increasing research interests [7-9]. Such materials feature a layered structure of alternative stacking LaO rock salt with ABO₃ perovskite. The relatively open lattice allows for a wide range of hyperstoichiometric oxygen in the interstices of LaO layers, resulting in high oxygen ion diffusion coefficients (*D*) [6, 10]. Compared to the prevalent Co-based perovskite IT cathodes, such as (LaSr)(CoFe)O_{3-δ} (LSCF), lanthanum nickelates possess mild thermal expansion coefficients (TEC) which matches better with current IT electrolytes like La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-δ}, Ce_{1-x}Gd_xO_{2-δ}, and cause no concerns associated with Co volatility, thus promising advantages in the dimensional and chemical stability during long-term operation [11]. In order to optimize the performance of nickelate materials, electrical/electrochemical modification has been carried out extensively on the pristine composition La₂NiO_{4+δ}. For instance, Ba, Sr for the A site and Cu, Fe for the B site were doped into LNO to adjust the catalytic activity and/or electrical conductivity, yielding major improvements [12-13]. Nevertheless, despite those advances, electrode performances from those LNO-based materials so far are still not as competitive as Co-based perovskite [14-15]. More investigations are needed to enhance the electrochemical activity for ORR of those R-P phase materials.

Compared with other cathodes, such as GdBaCo₂O_{5+δ} or LSCF, LNO in fact possesses similar *k*×*D* value in the IT region [16]. However, *k*/*D* for LNO is about 1 order of magnitude lower than most other cathodes. The relatively smaller *k* leads to a big oxygen diffusion length in the practical porous electrode since the surface exchange kinetics is comparatively slower than the bulk diffusion, which indeed gives rise to a broader surface reaction area but at the expense of larger diffusion resistance. It was confirmed in our previous study that LNO was limited by both

the surface exchange and bulk diffusion processes [7]. As a result, enhancement of the surface exchange process will not only increase the exchange rate but also reduce the resultant diffusion resistance [7, 17].

Among the surface kinetics studies on LNO [12, 18-20], to the best of our knowledge Mn as a likely dopant for the LNO has never been reported before. For the Mn-based perovskite, it has been found recently on LSM that the oxygen dissociative adsorption is a highly facile process without energy barrier [21-22]. The surface exchange kinetics for LSM is suppressed by the subsequent incorporation process due to the lack of surface vacancy in LSM [23]. In view of the similarity in the closest surroundings of B site in the perovskite and R-P phase, the surface adsorption activity of Mn in perovskite could be transferred to LNO to promote the sluggish surface exchange step. When operating in the IT region, the adsorption can be even more thermodynamically favorable than at high temperature because of the exothermic nature of this process. Such tendency cooperatively coupled with abundant surface oxygen defects and excellent bulk diffusion of LNO host can potentially endow Mn-doped LNO with great electrocatalytic activity. Inspired by this idea, substitution of Mn for Ni in LNO is carried out for the first time in this study. Sr is also doped into La site for the electrical conductivity improvement. $\text{La}_{2-2x}\text{Sr}_{2x}\text{Ni}_{1-x}\text{Mn}_x\text{O}_{4+\delta}$ (LSNM) was prepared and examined by electrochemical impedance spectroscopy (EIS) with well-defined dense layer and practical porous structure configurations to assess the surface exchange activity and electrode performance respectively. The results demonstrate that Mn doping improves the surface kinetics and electrode performance of LNO remarkably, proving LSNM a new superior ORR electrocatalyst for IT-SOFCs.

2. Experimental

2.1 Preparation of pure phase powder

$\text{La}_{2-2x}\text{Sr}_{2x}\text{Ni}_{1-x}\text{Mn}_x\text{O}_{4+\delta}$ ($x=0, 0.075, 0.1, 0.2, 0.3$, denoted as LNO, Sr15Mn7, Sr20Mn10, Sr40Mn20, Sr60Mn30) and $\text{La}_{1.85}\text{Sr}_{0.15}\text{Ni}_{0.95}\text{Mn}_{0.05}\text{O}_{4+\delta}$ (Sr15Mn5) were synthesized by ethylenediaminetetraacetic (EDTA)-citric sol-gel method described in details elsewhere [24]. For LSNM with $\text{Mn} \leq 10$ at.%, powders were intermediately ground between calcination cycles. The final phase structure was examined by X-ray diffraction (XRD, PANalytical X'pert PRO, Cu K α radiation).

2.2 Fabrication of symmetrical cells

A spray-modified pressing method was used to fabricate the dense thin layer LSNM [25-26]. The resultant powders mixed with polyvinyl butyral (PVB) and fish oil at the ratio of 100:2:1.5 wt. were ball-milled for 24 h to make ethanol suspension (5 g powders to 30 mL ethanol). The suspension was sprayed onto $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ (LSGM, powder from Fuel Cell Materials Co.) by air-brush (Master Airbrush G233 set) to produce electrolyte-supported thin layer symmetrical cells. The original thickness of LSNM layers was 80~100 μm . LSNM/LSGM/LSNM sandwiches were sintered to 1300°C for 4 h for densification. To eliminate possible element enrichment on the surface, the sintered pellets were polished manually using grinding papers then polishing cloth. The final electrode thickness is 30~70 μm depending on individual samples. Silver O-ring was attached to the electrode surface concentrically by silver paste as the lead wire. The chemical compatibility between LSNM and LSGM was checked by XRD through the mixture of Sr60Mn30 and LSGM powders at 1:1 wt. heated to 1300°C for 4 h.

For the porous symmetrical cells fabrication, cathode slurry was screen-printed onto both sides of LSGM pellets. To make the cathode slurry, the as-prepared powders were mixed with an ink vehicle (Fuel Cell Materials Co.) at the ratio of powders:vehicle=10:11 wt., then ground in a mortar until homogeneous slurry was obtained. The electrolyte pellets were fabricated by dry-pressing 0.7 g LSGM powder in a 16.5 mm stainless steel die under 300 MPa, followed by sintering at 1400°C for 4 h in air. The symmetrical cells were sintered at 1000°C for 2 h. The platinum paste was used as the current collector, silver wire as the lead wire.

2.3 Characterizations

The electrical conductivity of LSNM was measured in air through the 4 point DC Van der Pauw method. Each sample was uniaxially pressed into disc 16.5 mm in diameter 1mm in thickness and sintered at 1350°C for 4 h. The oxygen stoichiometry of those samples was determined by iodometric titration [27]. The electrocatalytic characterization of dense layers and porous samples was performed via EIS using Metrohm Autolab b.v. at open circuit condition over the frequency range from 0.01 Hz to 1 MHz. AC perturbation was set to 10 mV. The resultant spectra were deconvoluted using Z-view software. The microstructure of post-test samples was inspected by scanning electron microscope (SEM, Hitachi S-4700).

3. Results and Discussion

Fig. 1 (a) XRD of $(\text{La}_{2-2x}\text{Sr}_{2x})(\text{Ni}_{1-x}\text{Mn}_x)\text{O}_{4+\delta}$ samples synthesized at different temperatures and mixture of $(\text{La}_{1.4}\text{Sr}_{0.6})(\text{Ni}_{0.7}\text{Mn}_{0.3})\text{O}_{4+\delta}$ and $(\text{LaSr})(\text{GaMg})\text{O}_{3-\delta}$ calcined at 1300°C, (b) electrical conductivities of $(\text{La}_{2-2x}\text{Sr}_{2x})(\text{Ni}_{1-x}\text{Mn}_x)\text{O}_{4+\delta}$ in air from 100-800°C; inset shows the electrical conductivity of $\text{La}_{1.6}\text{Sr}_{0.4}\text{MnO}_{4+\delta}$ from the work of Munnings et al [28].

Fig. 1(a) shows the phase purity of synthesized powders. XRD patterns for all samples correspond to the R-P structure (PDF 11-0557). The synthesis temperature to obtained pure phase at different doping levels varies and is marked along. From the compatibility examination, no observable reaction is found in the mixture of Sr60Mn30 and LSGM (PDF 52-0022), proving good compatibility between LSNM and the LSGM electrolyte.

Fig. 1(b) exhibits the electrical conductivity of LSNM. Mn doping decreases the conductivity. For LNO, the electrical conductivity is thermally activated at low temperature as semiconductor, but thermally deactivated like metal when the temperature is higher than $\sim 400^\circ\text{C}$ [29]. For the Mn-based R-P phase $(\text{LaSr})_2\text{MnO}_{4+\delta}$, poor conductivity has been reported in the literature with the maximum less than 10 S/cm until 900°C [28]. The electrical conductivities of LSNM with $\text{Mn} \leq 10$ at.% in the present work show a similar trend of the pure LNO, but display a semi-conducting property as $(\text{LaSr})_2\text{MnO}_{4+\delta}$ at higher Mn contents. In the practical cathode with porous structure (assuming electrode thickness $l=50 \mu\text{m}$ and $\sigma_{\text{porous}}=0.1\sigma_{\text{dense}}$, then $RS = \frac{l}{\sigma_{\text{porous}}} = \frac{10l}{\sigma_{\text{dense}}}$), the specific ohmic resistance (RS) can be calculated less than $0.0025 \Omega\text{cm}^2$ in $600\text{-}800^\circ\text{C}$ for Sr15Mn5, Sr15Mn7 and Sr20Mn10 samples, which in most cases is negligible compared to the typical IT cathode polarization resistances.

Fig. 2 SEM images of the cross-section of (a) $(\text{La}_{1.85}\text{Sr}_{0.15})(\text{Ni}_{0.925}\text{Mn}_{0.075})\text{O}_{4+\delta}$, (b) $(\text{La}_{1.8}\text{Sr}_{0.2})(\text{Ni}_{0.9}\text{Mn}_{0.1})\text{O}_{4+\delta}$ and (c) $(\text{La}_{1.6}\text{Sr}_{0.4})(\text{Ni}_{0.8}\text{Mn}_{0.2})\text{O}_{4+\delta}$ -LSGM bilayers, and (d) the microstructure of $(\text{La}_{1.8}\text{Sr}_{0.2})(\text{Ni}_{0.9}\text{Mn}_{0.1})\text{O}_{4+\delta}$ porous electrode.

Fig. 2(a)-(c) show the cross-sectional SEM of LSNM/LSGM samples. Dense structure except for few closed pin holes was obtained after 1300°C sintering. A good adhesion between LSNM and LSGM is confirmed. No visible chemical reaction can be observed in the interface area, which is consistent with the XRD results. The thickness of LSNM dense layers (30-50 μm) are much smaller compared to the characteristic length for lanthanum nickelates in the IT region, that is, 1400-1700 μm [6, 19], ensuring that the bulk diffusion resistance would be marginal relative to the surface exchange resistance in the dense layer samples. Fig. 2(d) shows the microstructure of Sr20Mn10 electrodes. Suitable porosity and good bond between electrode and electrolyte are obtained.

Fig. 3 (a) EIS of $(\text{La}_{2-2x}\text{Sr}_{2x})(\text{Ni}_{1-x}\text{Mn}_x)\text{O}_{4+\delta}$ dense layer cells at 700°C in air, (b) the Arrhenius plot of the equivalent k values for $(\text{La}_{2-2x}\text{Sr}_{2x})(\text{Ni}_{1-x}\text{Mn}_x)\text{O}_{4+\delta}$ calculated from R_{surf} in 600-800°C.

Fig. 3(a) shows the EIS arcs for LSM dense layer cells. To accurately assess the surface kinetics of cathode materials, dense thin layers have been widely adopted in the literature in order to avoid bulk diffusion influence and complex microstructure of the porous electrode. An equivalent circuit (EC) derived by Jamnik et al.[26, 30] for surface exchange process in dense layer samples is presented in Fig. 3(a). In this EC, the single arc formed by the combination of a chemical capacitance (C_{chem}) and a surface exchange resistance (R_{surf}) is responsible for the surface reaction process. The spectrum of Sr15Mn5 shows a single arc profile and can be fitted into this EC satisfactorily, consistent with the surface dominant situation. The rest samples share the similar profile and were fitted into this EC also.

The corresponding surface exchange coefficient (k) is calculated from the R_{surf} through Eq. 1 [31-32],

$$k = \frac{RT}{4F^2 R_{\text{surf}} c_o} \quad (1)$$

where F is the Faraday's constant, c_o the oxygen concentration in LSM, R and T remain the universal physical meanings. Fig. 3(b) displays the Arrhenius plot of k values for LSM. The exchange rate ranks as Sr20Mn10>LNO>Sr15Mn7>Sr15Mn5>Sr40Mn20>Sr60Mn30. k for Sr20Mn10 is about twice bigger than that of LNO. To assess the real effect of Mn on the surface exchange, both Sr and Mn need to be taken into account in the evolution of k . As stated before, although Mn is the designed substitute for Ni, Sr is used to improve the electrical conductivity. It has been demonstrated previously that Sr doping impairs the surface kinetics of LNO by increasing the oxidation state of Ni and reducing interstitial oxygen population [7, 26, 33]. Thus, the improvement from Mn doping could be partially offset by Sr. To clarify the real cause, Sr15Mn5 sample was prepared. Comparing Sr15Mn5 to Sr15Mn7, with the fixed Sr content, k is increased from 3.7×10^{-7} to 6.9×10^{-7} cm/s at 700°C by the extra 2.5 at.% Mn content in Sr15Mn7, which ambiguously proves the advantageous effect of Mn in the surface exchange process. The apparent activation energy (E_a) is derived based on this Arrhenius plot. LNO shows a varying E_a , 0.97-1.21 eV, which can be assigned to the reduction of δ with increasing temperature [26]. E_a for Mn $\leq$ 10 at.% samples is roughly the same, but decreases in the ones with higher Mn content. Table 1 shows the oxygen stoichiometry for those LSM. LNO possesses the highest interstitial oxygen amount. As this species is crucial to the ion incorporation [7, 26], the loss of interstitial oxygen may result in a retarded overall reaction. However, the surface kinetics of Sr20Mn10 is

faster than LNO. It probably indicates that the improvement in the dissociative adsorption process outweighs the detrimental effect on the ion incorporation step after Mn doping. With higher dopant content, the interstitial oxygen for Sr40Mn20 decreases to 1/3 of that for Sr20Mn10, and even becomes negative in Sr60Mn30. Considering such small population of interstitial oxygen, the incorporation process in Sr40Mn20 and Sr60Mn30 could be more rate-limiting than the dissociative adsorption step. As a result, the surface reaction kinetics will be determined by the incorporation step in those samples. This transition of rate-limiting step from dissociative adsorption-dominant to ion incorporation-dominant is most probably responsible for the change of E_a in Fig. 3. In consequence, an optimum Mn content should be the one balancing the rate limitation from dissociative adsorption and ion incorporation. It is noteworthy that E_a in Fig. 3 are smaller compared to those obtained from $(\text{LaSr})_2\text{MnO}_{4+\delta}$ porous electrodes in the literature (1.39-1.55 eV) [34]. The cause for this discrepancy lies in the change of reactive area in the porous samples. The apparent activation energy of the porous $(\text{LaSr})_2\text{MnO}_{4+\delta}$ electrodes comprises not only the intrinsic energy barrier of the reaction but also the contribution from the enlargement of reactive areas from the bulk pathway. Therefore, as temperature increases, the performance gain consists of the contributions from both thermal activation and augmentation of reactive sites, leading to a larger E_a . In fact, it is found that E_a for the porous Sr20Mn10 electrode (as will be shown in Fig. 4) can be calculated as 1.57 eV, which is in agreement with the above values in the literature.

Table 1 Oxygen content in $(\text{La}_{2-2x}\text{Sr}_{2x})(\text{Ni}_{1-x}\text{Mn}_x)\text{O}_{4+\delta}$ samples determined by iodometric titration, based on parallel experiments with a reproducibility of ca. ± 0.01 .

Sample	LNO	Sr15Mn5	Sr15Mn7	Sr20Mn10	Sr40Mn20	Sr60Mn30
δ	0.143	0.068	0.097	0.086	0.030	-0.113

Table 2 Comparison of k for common R-P phase cathodes at 700°C

	k (cm/s)	E_a (eV)	Ref.
Sr20Mn10	1.57×10^{-6}	1.01	This work
$\text{La}_2\text{Ni}_{0.9}\text{Co}_{0.1}\text{O}_{4+\delta}$	1.41×10^{-6}	0.60	[19]
$\text{Pr}_2\text{NiO}_{4+\delta}$	1.0×10^{-6}	0.77	[35]

LNO	8.6×10^{-7}	0.97-1.21	This work
$\text{La}_2\text{Ni}_{0.9}\text{Fe}_{0.1}\text{O}_{4+\delta}$	4.0×10^{-7}	1.39	[12]
$\text{La}_{1.8}\text{Sr}_{0.2}\text{NiO}_{4+\delta}$	2.7×10^{-7}	1.06-1.37	[26]
$\text{Nd}_{1.8}\text{Ca}_{0.2}\text{NiO}_{4+\delta}$	1.5×10^{-7}	1.35	[35]
$\text{La}_2\text{CuO}_{4+\delta}$	8.0×10^{-8}	0.57	[13]
$\text{La}_2\text{Cu}_{0.5}\text{Ni}_{0.5}\text{O}_{4+\delta}$	6.5×10^{-9}	1.20	[13]

Table 2 summarizes several most commonly used R-P phase cathodes. Sr20Mn10 from this work exhibits one of the highest k values, 1.57×10^{-6} cm/s at 700°C, which is much better than its Co, Fe and Cu-doped counterparts, demonstrating the notable advantage of Mn over other dopants.

Fig. 4 Comparison of polarization resistances for $\text{La}_2\text{NiO}_{4+\delta}$ (square) $\text{La}_2\text{NiO}_{4+\delta}/(\text{La}_{0.8}\text{Sr}_{0.2})_{0.95}\text{MnO}_{3-\delta}$ (circle) and $(\text{La}_{1.8}\text{Sr}_{0.2})(\text{Ni}_{0.9}\text{Mn}_{0.1})\text{O}_{4+\delta}$ (triangle) at (a) 650°C, (b) 700°C and (c) 750°C.

Fig. 4 shows the ohm-subtracted impedance for the related porous electrode at different temperatures. Sr20Mn10 sample yields much better performance relative to that of LNO. At 750°C in Fig. 4(c), R_p is 0.74 Ωcm^2 for LNO and 0.42 Ωcm^2 for Sr20Mn10, accounting for a ~75% enhancement after Mn doping. For the purpose of comparison, the cathode consisting of physically mixed LNO and LSM powders at 9:1 wt. ratio was also measured. Such composite cathode shows better performance than LNO, confirming the previous speculation that improvement of surface exchange will benefit the ORR process substantially on LNO. But it is still not as active as the atomically homogenous catalyst Sr20Mn10, most probably because that the enhanced surface reaction zone in the composite cathode is still limited to the LSM/LNO interface but expanded to the entire surface of Sr20Mn10 owing to the high ionic conductivity of the LNO host. In fact, the electrode performance for Sr20Mn10 is the highest among those $\text{La}_2\text{MO}_{4+\delta}$ -related IT cathodes ever reported in the literature, such as Cu[20, 36], Co[37-38] and Ni[8, 14-15]-based R-P phase materials. Those results prove that the excellent surface exchange activity of Mn and the high ionic conductivity of R-P phase structure have been synergistically combined through element doping, producing a new IT cathode material with outstanding performance.

At last, since the Sr/Mn=2 ratio was empirically chosen, higher surface and electrode activity could be reasonably expected through a systematical study of Sr content in the future.

4. Conclusions

Mn doping in $(\text{La}_{2-2x}\text{Sr}_{2x})(\text{Ni}_{1-x}\text{Mn}_x)\text{O}_{4+\delta}$ ($0.05 \leq x \leq 0.3$) was investigated to enhance the surface exchange kinetics and electrode performance of the IT cathode. Pure R-P phase was obtained for Mn & Sr-doped LNO. The surface exchange resistance was evaluated by EIS on the dense thin layer structure. A superior result was obtained from Sr20Mn10 with $k=1.57 \times 10^{-6}$ cm/s at 700°C in air, ~80% higher than that for the pristine LNO. Of the most commonly used R-P phase cathode materials, Sr20Mn10 displays one of the highest k values. The corresponding electrode performance was measured with practical porous structure. It was remarkably promoted as well. R_p for LNO was 0.74 Ωcm^2 at 750°C, but decreased significantly to 0.42 Ωcm^2 for Sr20Mn10. Composite LNO/LSM cathode was also measured to justify the effectiveness of doping. Sr20Mn10 exceeded the composite cathode by ~50% in performance. Compared to other $\text{La}_2\text{MO}_{4+\delta}$ IT cathodes, Sr20Mn10 yielded a highly competitive performance ever reported in the

literature. Such results demonstrate that Mn doping successfully exploits the synergic effect related to the high surface activity of Mn and bulk diffusivity of LNO, yielding a new ORR electrocatalyst with excellent performance for IT-SOFCs.

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