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Tailoring of surface modified ultrathin membranes with CO_2 tolerance and high oxygen permeability

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Table S1 lists the lattice parameters of $(Pr_{0.9}La_{0.1})_2(Ni_{0.74}Cu_{0.21}Nb_{0.05})O_{4+\delta}$ (PLNCN) powders derived from Rietveld refinements. The values of wRp and Rp indicated that the structure model we applied satisfied with the penalty error limit and the synthesized PLNCN powders were pure without any other impurity phase.

Table S1 Estimated lattice parameters of PLNCN powders sintered at 1000 °C for 3 h by Rietveld method.

Space group	*a* (Å)	*c*(Å)	*V* (Å)^3	*δ*	wRp	Rp
I4/*mmm*	3.83813(3)	12.55409(4)	184.9373	0.232(3)	7.37%	5.62%

Figure S1 shows the X-ray patterns of PLNCN dense disk sintered at 1300 °C for

5 h. The PLNCN disk also presented a tetragonal I4/mmm K2NiF4-type structure, indicating the phase structure of PLNCN did not change obviously after the high-temperature sintering process.

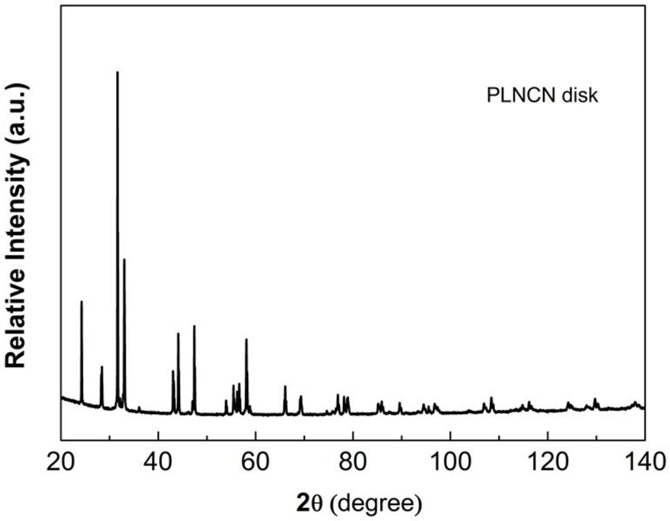


Figure S1. X-ray diffraction patterns of PLNCN dense disk sintered at 1300 °C for 5 h.

Figure S2 presents the electrical conductivities of PLNCN sample measured in air from 300 °C to 900 °C via a four-probe method. As the electronic conductivities of Ruddlesden-Popper MIEC oxides are much more than one magnitude higher than the oxygen ionic conductivities, the measured electrical conductivities can be mainly referred to electronic conductivities. The electrical conductivities of PLNCN initially increased with temperature until reaching a maximum of 80.4 S cm^{-1} at 450 °C, and then decreased when further increasing the testing temperature, which indicated that the conductivities of PLNCN presented a p-type conducting behavior. The decrease of conductivities was caused by the loss of the interstitial oxygen so as to the reduce of carrier density. The conductivity obtained for the PLNCN oxide at the operation temperatures of oxygen transporting membranes (OTMs) exhibited a significant level.

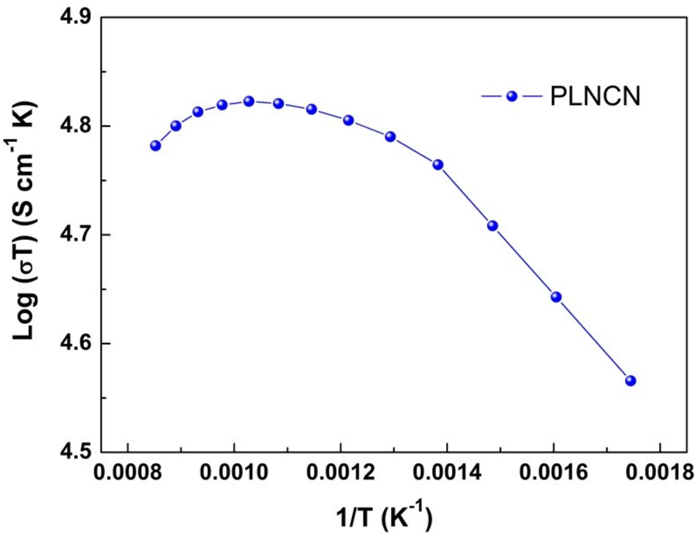
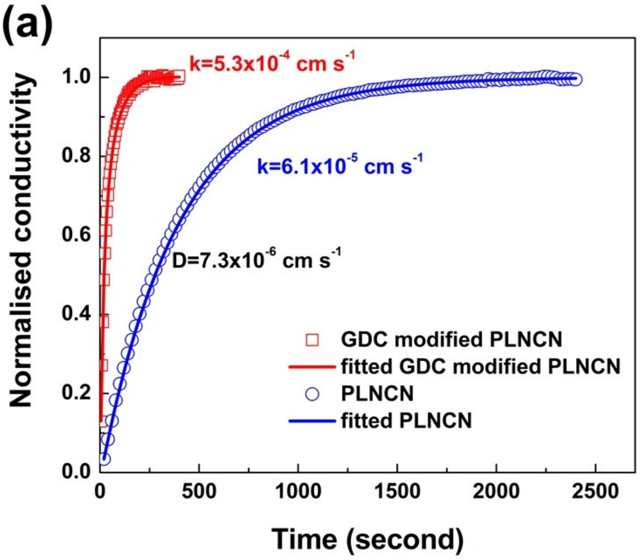


Figure S2. Electrical conductivities of PLNCN dense bar samples measured in air from 300 °C to 900 °C.

The oxygen surface exchange kinetics of pure PLNCN and GDC modified PLNCN were studied,[1-3] in order to identify the effect of GDC coating on surface activity. Measurement of oxygen surface exchange coefficient, k_{chem}, were typically performed using electrical conductivity relaxation (ECR) method,[4-7] which was based on the principle that a variation of oxygen partial pressure in the ambient atmosphere could bring in an accordingly change in the oxygen defect concentration of the MIEC oxides. The measurement device had been illustrated in our previous work.[8] In this study, the PLNCN dense bar samples with the dimensions of 2.5 mm × 7.0 mm × 0.65 mm were prepared. The obtained PLNCN bars were infiltrated with the 0.1 M GDC solution, and then heat-treated at 900 °C for 1 h to load GDC nano particles onto the PLNCN surfaces.

Figure S3a shows the electrical conductivity relaxation profiles of PLNCN and GDC modified PLNCN samples at 600 °C upon abruptly changing the oxygen partial pressure from 0.01 to 0.05 atm. It was reported that the Pr_2NiO_4-type materials are not stable under high oxygen partial pressure.[9, 10] In this case, the low oxygen partial pressure probably maintained the stability of PLNCN. The relaxation time of pure PLNCN samples at 600 °C was about 2500 s. It decreased to 400 s after the modification of GDC. The oxygen ionic transport properties through PLNCN bulk should not be affected by the surface coating. It was therefore reasonable to foresee that the change in relaxation time was caused by the variation on surface exchange process. The lower relaxation time indicated the higher surface exchange dynamics. The fitted surface exchange coefficients (k_{chem}) of PLNCN and GDC modified PLNCN samples are shown in Figure S3b. It was clear that the coating of GDC particles on PLNCN surface can substantially accelerate the chemical oxygen surface exchange coefficient (k_{chem}). For example, the k_{chem} of PLNCN at 600 °C was 6.1×10^{-5} cm s^{-1}. It increased to 5.3×10^{-4} cm s^{-1} when GDC was introduced, which was nearly one magnitude higher than that of pure PLNCN. Similar effects of doped ceria modification on oxygen vacancy type of perovskites had widely reported, such as $La_{0.8}Sr_{0.2}MnO_{3-\delta}$,[2] $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$,[3] and $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$[1] oxides. In this study, the enhancement of surface exchange process on oxygen interstitials type of PLNCN oxide was also demonstrated, which might due to the synergistic action of GDC and PLNCN oxides for oxygen incorporation. Several reports had systemically studied the enhancement effect at interface. For example, Wang et al.[11] pointed out that oxygen exchange and bulk diffusion process appears to be dominated by the interface of $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ (SFM) and $Sm_{0.2}Ce_{0.8}O_{2-\delta}$ (SDC) rather than the single phase SFM or SDC. Lin et al.[12] also demonstrated that the ionic conductivity in the interface of $Gd_{0.2}Ce_{0.8}O_{2-\delta}$ (GDC) and $CoFe_2O_4$ (CFO) composite is significant. In current study, much interface of PLNCN and GDC was created after surface modification. The introduction of GDC particles and interface of PLNCN-GDC could significantly improve the oxygen-ionic conduction on PLNCN surface so as to the oxygen reduction reaction process. Moreover, the activation energy of k_{chem} of PLNCN and GDC modified PLNCN samples were 1.42 and 1.02 eV. The reduced activation energy by GDC modification indicated again the changed oxygen reduction mechanism.



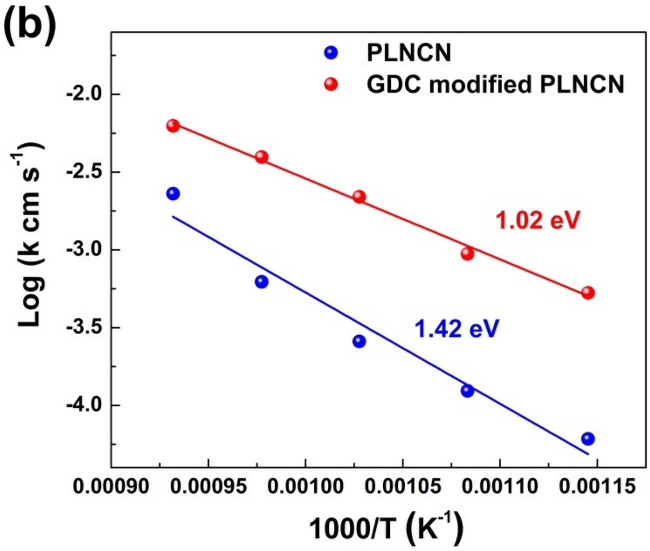


Figure S3 (a) Electrical conductivity relaxation of PLNCN and GDC modified PLNCN bar samples measured at 600 °C with the oxygen partial pressure changed from 0.01 to 0.05 atm, (b) Fitted surface exchange coefficients of PLNCN and GDC modified PLNCN as a function of temperature.

Figure S4 provides thermogravimetric (TG) curves of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) and PLNCN in the presence of pure CO_2 atmospheres. The samples were heated with ramp rates of 10 °C min^{-1} up to 1000 °C with CO_2 flow rate of 50 mL min^{-1}. For the TG of BSCF powders, about 4.6% mass loss of BSCF was observed when the temperature was below 500 °C. Then, the mass of BSCF sample started to increase at about 500 °C and continued to increase till 942 °C with the mass value of 102.1%, which was attributed to the formation of carbonate, such as $BaCO_3$. Further increasing the temperature could lead to the decomposition of carbonate. However, in the case of PLNCN oxides, the mass of PLNCG continuously decreased with the increase of temperature. The weight loss of PLNCN powders under CO_2 atmospheres may be attributed to desorption of oxygen atoms in lattice. No sharp weight increase or loss of the PLNCG sample suggested that no carbonates generated or decomposed during the temperature increasing. The results demonstrated the good chemical stability of PLNCN against CO_2.

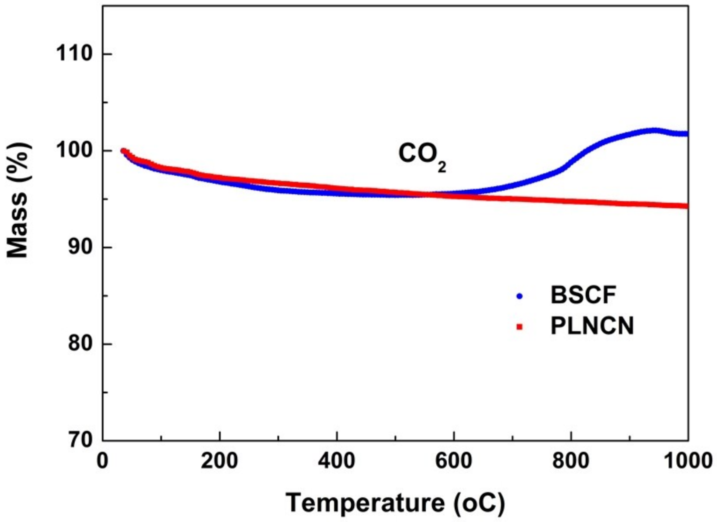


Figure S4 Thermogravimetric curves of BSCF and PLNCG powders under pure CO_2 atmosphere.

Figure S5a shows the XRD spectra of GDC modified PLNCN membrane after test in the presence of CO_2 atmosphere for 200 h. A tiny peak around 36 ° was obtained, indicating the impurity of $GdCu_2O_4$ (PDF-87-1746) might be formed after long term operation. Figure S5b is the cross-section view of GDC modified PLNCN membrane after test. There were no obviously changes in the membrane structure.

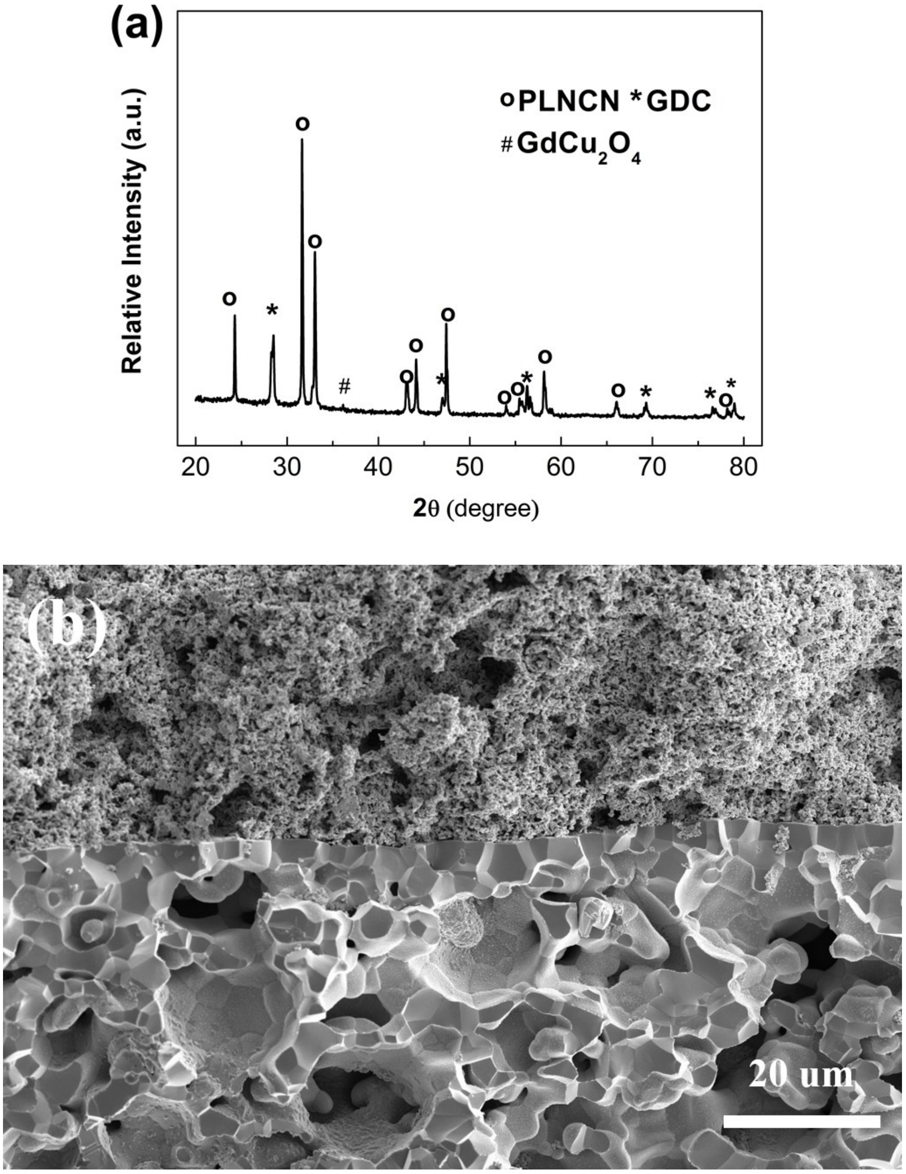


Figure S5 (a) XRD partners and (b) SEM image of GDC modified PLNCN membrane after CO_2 tolerance test

Acknowledgment

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