



Short communication

Investigate the proton uptake process of proton/oxygen ion/hole triple conductor $\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.1}\text{Y}_{0.1}\text{O}_{3-\delta}$ by electrical conductivity relaxation

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HIGHLIGHTS

- Proton uptake kinetic was determined by electrical conductivity relaxation.
- The proton surface exchange coefficient of BCFZY is $3.85 \times 10^{-6} \text{ cm}^{-1}$ at 500°C .
- The proton uptake kinetic could be accelerated greatly by doped ceria.

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ABSTRACT

The proton surface uptake kinetics of proton, oxygen ion and hole triple conductor $\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.1}\text{Y}_{0.1}\text{O}_{3-\delta}$ (BCFZY) is investigated by electrical conductivity relaxation method (ECR). The proton uptake process is controlled by changing the water partial pressure at constant temperature. And the proton concentration in BCFZY bulk could be calculated by the conductivity change value ($\Delta\sigma$: 0.063 Scm^{-1} at 500°C) from 0% to 10% pH_2O . The proton surface exchange coefficient, k^0 is $3.85 \times 10^{-6} \text{ cm}^{-1}$ at 500°C , derived from fitting the relaxation curve. It is also found the proton uptake reaction rate would be enhanced under higher oxygen partial pressure. And the k^0 value could be greatly enhanced by one order of magnitude with doped ceria coated on BCFZY surface, which also proved that the proton uptake kinetics is limited by the surface exchange step. In all, this work provides an effective way to measure the proton surface exchange kinetic for proton conductive cathode.

1. Introduction

Protonic ceramic fuel cells (PCFCs) have a good application prospect because of its low ionic transport activation energy compared to that of oxygen ion conductor at low temperature [1]. And in PCFC cathodes, mixed ion/electron conductor cathode materials have received extensive attention because of their ability to increase the air/electrode/electrolyte three phase boundary length and thus increase the rate of oxygen reduction reaction [2–4]. But compared to oxygen ion fuel cell, the proton transport ability is the key factor to improve the cathode performance due to the reaction of proton with air to form water in cathode side [5,6]. And in proton conductor materials will only show the property of conducting proton in the atmosphere containing water or hydrogen, where water dissociates and forms proton defects with oxygen and oxygen vacancy, respectively [7,8]. Take these factors

into account, cathodes materials for PCFC are desired with high electron/hole and proton conductivity [9].

To achieve better cell performance, the cathode materials need to show a certain proton conductivity, and proton conductivity up to 10^{-5} Scm^{-1} can have sufficient electrode activity in an estimated model [10]. Therefore, the concentration and rate of proton formation in cathode materials are also the key factors affecting the performance of cathode materials. The accurate measurement of the proton surface exchange rate in the cathode material has important reference for its application in PCFC. But it is very difficult to directly measure the proton conductivity of the cathode, and quantitative analysis of oxygen ion/proton/hole mixed conductivity is also a big challenge, while actually it is almost impossible to determine the proton conductivity at a certain temperature and partial pressure atmosphere [10]. The direct measurement of protonic conductivity needs the suppression of the predominant

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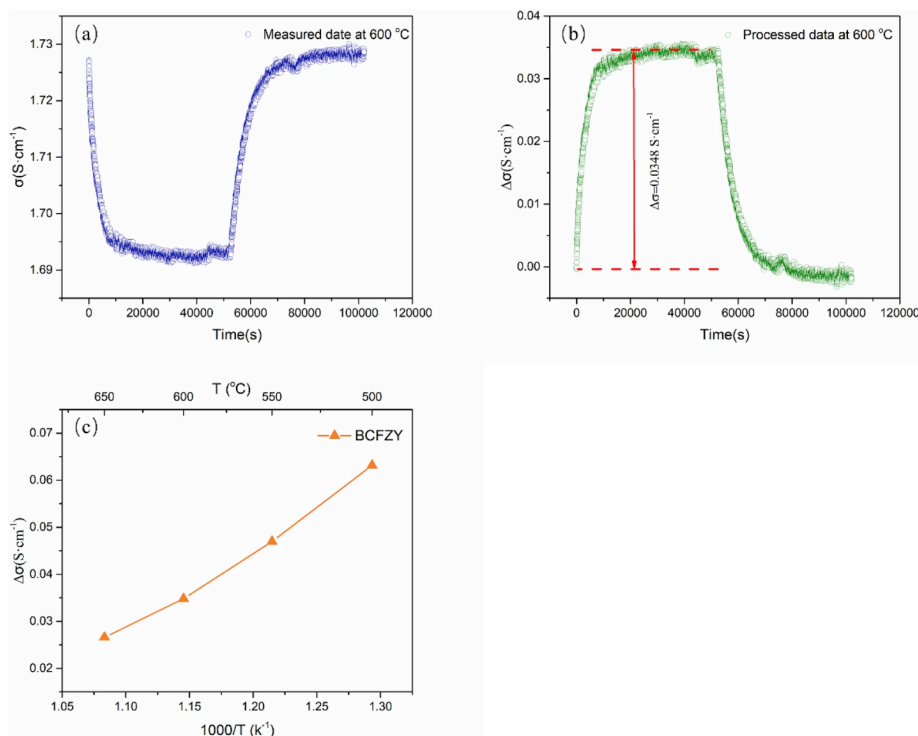


Fig. 1. (a) Exemplary conductivity relaxation curve of BCFZY sample upon atmosphere changes from the dry air (0% H₂O) to 10% H₂O partial pressure and then switched to the dry environment at 600 °C, (b) the simplified conductivity relaxation curve at 600 °C and (c) the net conductivity changes of BCFZY measured at different temperatures.

electronic conductivity which is difficult, as the electronic carriers are very mobile compared to ionic species. And even with the method of secondary ion mass spectrometry, the accurate concentration of proton defects in materials still cannot be accurately detected. At the same time, the generation of protons in the cathode material must rely on the existence of water in the external environment.

In proton conductor, proton uptake is carried out by the combination of H₂O or H, thus the corresponding proton defect concentration change in cathode bulk can be measured through thermogravimetric measurement as reported in research work [8]. Poetzsch et al. measured the proton uptake process of Ba_{0.5}Sr_{0.5}Fe_{0.8}Zn_{0.2}O_{3- δ} by mass relaxation method and gave a calculated proton conductivity, a boundary of $0.9\text{--}3 \times 10^{-4}$ Scm⁻¹ [9]. Zohourian et al. also found that the proton concentration of Ba_{0.95}La_{0.05}Fe_{0.8}Zn_{0.2}O_{3- δ} is 10% per formula unit at 250 °C, 5.5% at 400 °C, 2.3% at 500 °C [8]. All of these works proves the weight relaxation method to be an effective way to measure the proton uptake process for mixed conductor, but it still can't be used to determine the effect additional phase on proton uptake process since thermogravimetric could not separate the weight change from the mixed conductor and surface coating phase.

In the past reports, electrical conductivity relaxation (ECR) technique can quantitatively determine the oxygen incorporate and oxygen ion diffusion process in mixed conductor materials [11]. Bouwmeester et al. demonstrated the measurement the oxygen surface exchange coefficient of pure La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3- δ} (LSCF) by ECR [12]. And Hu et al. employed ECR method to precisely achieve the amount of oxygen incorporated at the LSCF-Sm_{0.2}Ce_{0.8}O_{1.9}-gas three phase boundary [13]. For proton/hole/oxygen ion triple conductive material, BaCo_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1}O_{3- δ} (BCFZY), has been demonstrated with excellent power output performance and long term stability as PCFC cathode [1,14–17]. In this work, the ECR method was employed to measure proton surface uptake kinetics of BCFZY by changing water partial pressure. The concentration of proton defects in BCFZY was calculated. The proton surface exchange coefficient was derived from relaxation

curve measured by ECR. And doped ceria was demonstrated to could greatly accelerate the proton uptake process for BCFZY.

2. Experiment

2.1. BCFZY powder synthesis

BaCo_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1}O_{3- δ} (BCFZY) powder was synthesized by using a previously developed sol-gel method described elsewhere [14,18]. To conduct the ECR measurement, the BCFZY powders were pressed into a rectangular bar and sintered at 1200 °C for 5 h in air to form dense BCFZY bars with dimension size of 26.30 × 4.56 × 0.70 mm³. All sintered samples were confirmed to possess a density in excess of 95% of the theoretical density determined using the Archimedes method. Sm_{0.2}Ce_{0.8}O_{1.9} (SDC) nanoparticles were coated on BCFZY bars surface by dropping SDC solution (Ce⁴⁺ and Sm³⁺ at the mole ratio of stoichiometry with appropriate amount of glycine) and then heated at 600 °C. In this experiment, the concentration of SDC solution we configured was 0.1 mol L⁻¹ and the amount of SDC coated on BCFZY surface was 0.03 mgcm⁻².

2.2. Electrical conductivity relaxation experiment and characterization

The conductivity was measured by a standard, four-probe method using a measurement system consisting of a digital multimeter (Keithley 2011) using the LABVIEW 8.5 software. In proton uptake measurements, the water partial pressure was controlled by humidifier (flowing the gas through a humidifier at 45 °C water temperature). And the samples were equilibrated at certain T and pO₂ (21%), and then p_{H₂O} was changed stepwise. The resulting p_{H₂O} values were calculated from the water vapor pressure at a given temperature. And electron magnetic valve was used to switch the gas tube from the dry atmosphere to the moisture air. Meanwhile, in order to explore the influence of oxygen partial pressure in this experiment, the proton uptake behavior of samples under

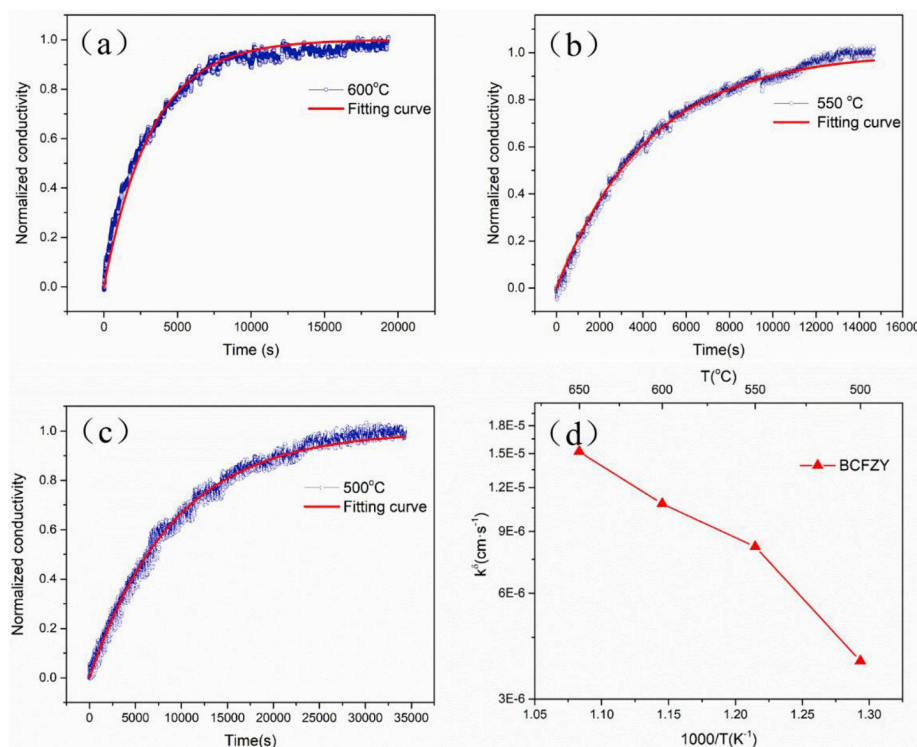


Fig. 2. (a-c) The normalized conductivity versus time of BCFZY at various temperatures and (d) the proton surface exchange coefficient k^s for BCFZY measured by ECR method from 500 to 600 °C.

different oxygen partial pressure (1%, 21% and 100%) at 650 °C. The moisture pressure transformation is completed in less than 20 s at a gas-flow rate of 100 ml min⁻¹. The surface morphology of BCFZY and SDC modified samples were observed by scanning electron microscope (SEM, Hitachi SU8020).

3. Results and discussion

3.1. Proton uptake reaction

In the perovskites like BCFZY containing oxygen vacancies and holes, the proton uptake can occur in two different reactions. And as suggested by Maier et al. [8,9,19], the proton uptake reaction can be described by two independent reactions:



Eq(1) is an acid-base reaction involving oxygen vacancy hydration when the vacancy concentration exceeds that of the electronic defects ($2[V_\text{O}^{\bullet\bullet}] > [h^\bullet]$). This reaction mainly targets to some low active electrolytes as Ba(Zr/CeY)O_{3-δ} and protons are transferred by lattice oxygen to form proton defects [9]. However, for some triple conductive materials with strong redox ability, redox/hydrogenation reaction as Eq.(2) will occur when they are exposed in a humid environment due to the large electronic defect concentration ($[h^\bullet] > 2[V_\text{O}^{\bullet\bullet}]$) at the expense of holes which is typical for a cathode perovskite. This is also explained by the boundary condition between the different predominant reactions from the general defect chemical model comprising the hydration and hydrogenation reaction [19–21]. Proton absorption can be carried out because of the sacrifice of holes where hydrogenation reaction could uptake, instead of hydration. And it is more favorable in PCFC working condition since electron/hole is continuous supplied by out circuit. Therefore, for some cathode materials like BCFZY that are mainly P-type conductors, proton uptake can be achieved by sacrificing of the holes in

a humid atmosphere [19], and then the change in electrical conductivity could be monitored to reflect the hydrogenation reaction. And with the hydrogenation reaction, more protons would incorporate into BCFZY lattice as well as more hole would be consumed. And finally, the hydrogenation reaction would arrive the equilibrium state where the proton concentration would be constant and it also means the conductivity would be a fixed value.

Fig. 1a shows a typical conductivity relaxation curve of the BCFZY upon changing the atmosphere from dry air (0% H₂O) to 10% H₂O water at 600 °C. The number of the experimental data points has been processed for simplicity. It is obvious that the curve is non-monotonic and the conductivity first decreases sharply with time upon the sample exposed to 10% H₂O atmosphere, then it slowly arrives equilibrium value. After the atmosphere was switched to dry air, the conductivity changes to the opposite direction and gradually reaches the original value which means the protons emerges to form holes. And the conductivity change in Fig. 1a is quite pronounced and totally reversible. Merkle et al. [14] also pointed out that in high oxygen partial pressure (21% O₂ in this work), the predominated contribution of proton uptake is hydrogenation as Eq(2).

Fig. 1b shows that the net conductivity change value is 0.0348 Scm⁻¹ for BCFZY from dry air to 10% H₂O at 600 °C. For p-type conductor materials, we can calculate its electrical conductivity in the following formula: $\sigma = [h^\bullet]e\mu$, where e is the electron charge, μ is the charge carrier hole mobility and $[h^\bullet]$ is hole concentration. In this work, ECR measurement was conducted at a constant temperature, so μ is a fixed value, and then $\Delta\sigma = \Delta[h^\bullet]e\mu$. So the proton concentration $[\text{OH}_\text{O}^\bullet]$ in BCFZY lattice could be calculated as: $\frac{\Delta\sigma}{\sigma} = \frac{[\Delta h^\bullet]e\mu}{[h^\bullet]e\mu} = \frac{[\Delta h^\bullet]}{[h^\bullet]} = \frac{\Delta[\text{OH}_\text{O}^\bullet]}{[h^\bullet]}$. In the dry air atmosphere, the initial proton concentration $[\text{OH}_\text{O}^\bullet] = 0$ where $\text{pH}_2\text{O} = 0$. So the final proton defect concentration at 10% H₂O, $[\text{OH}_\text{O}^\bullet] = \Delta[\text{OH}_\text{O}^\bullet] = [h^\bullet] \times \frac{\Delta\sigma}{\sigma}$, and the hole concentration could be achieved by Hall-effect measurement at high temperature since we still need to further explore this work.

Fig. 1c shows the $\Delta\sigma$ values from 500 °C to 650 °C. As we can see, the

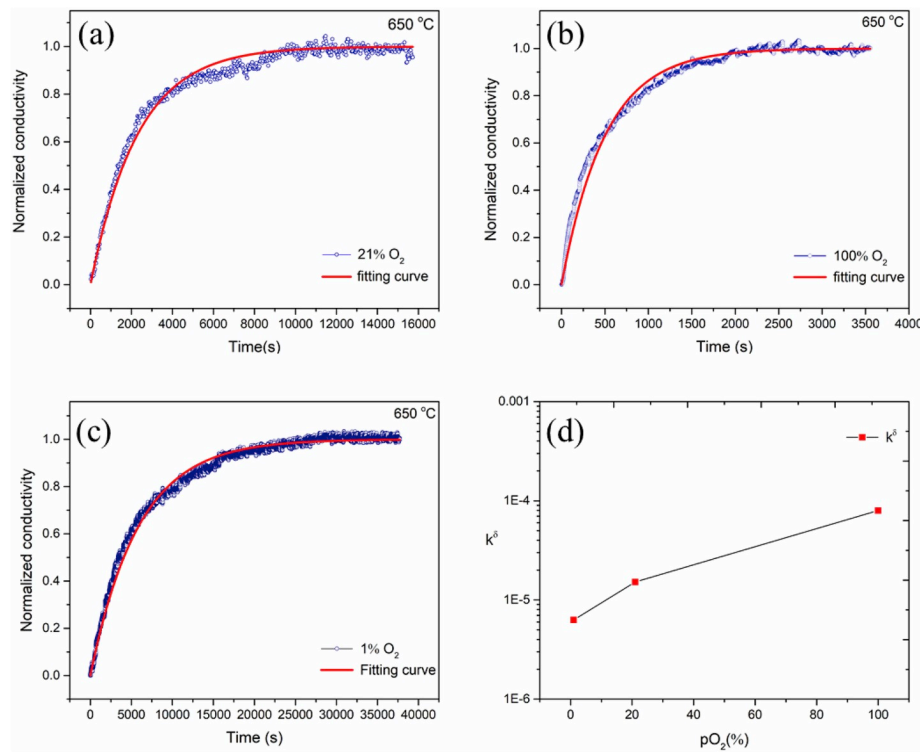


Fig. 3. (a–c) Treated normalized conductivity maps of BCFZY at different oxygen partial pressure and (d) the proton surface exchange coefficient k^δ for BCFZY derived by ECR method under several oxygen partial pressures at 650 °C.

$\Delta\sigma$ value decrease from 0.063 Scm^{-1} (500 °C) to 0.027 Scm^{-1} (650 °C). As discussed above, the $\Delta\sigma$ value is in a positive linear relationship with the final proton concentration in BCFZY bulk. So it could be concluded that the $[\text{OH}_o^\bullet]$ value is lower at higher temperature. And as pointed out by Merkle et al., the standard enthalpy of hydrogenation reaction is a negative value obtained from oxygen uptake enthalpy and hydration enthalpy [22,23], which explained the decreased incorporated proton concentration with temperature. And it is also consistent with reported lower proton concentration in higher temperature measured by mass relaxation [3,8–10,19].

3.2. Electrical conductivity relaxation

When the water partial pressure in the gas phase increases from $p\text{H}_2\text{O} = 0\text{--}10\%$, proton would incorporate into BCFZY until a new thermodynamic equilibrium state. The incorporation increases the proton concentration and thus reduces hole concentration as well as the electrical conductivity. With a linear relationship between the conductivity and proton concentration as in Eq.(2), the following equation is derived:

$$NC(t) = \frac{\sigma(t) - \sigma(0)}{\sigma(\infty) - \sigma(0)} = \frac{[h^\bullet]_t - [h^\bullet]_0}{[h^\bullet]_\infty - [h^\bullet]_0} = \frac{[\text{OH}_o^\bullet]_t - [\text{OH}_o^\bullet]_0}{[\text{OH}_o^\bullet]_\infty - [\text{OH}_o^\bullet]_0} \quad (3)$$

where $NC(t)$ is the dimensionless that represents normalized change in the conductivity/proton defect concentration [13]. $\sigma(t)$, $[h^\bullet]_t$ and $[\text{OH}_o^\bullet]_t$ are electrical conductivity, holes concentration and proton defect concentration at time t . $\sigma(0)$, $[h^\bullet]_0$ and $[\text{OH}_o^\bullet]_0$ are the corresponding initial values, and $\sigma(\infty)$, $[h^\bullet]_\infty$ and $[\text{OH}_o^\bullet]_\infty$ those at infinite time (equilibrium time) when the new thermodynamic equilibrium state is arrived.

Fig. 2a–c shows the normalized conductivity versus the incorporation time from 500 to 600 °C. It could be seen that the profile is typical for the ECR measurement. In the proton uptake reaction, water would firstly incorporate into BCFZY the surface (denoted as surface exchange coefficient k^δ) and then the defects migrate into BCFZY bulk with the

corresponding diffusion kinetics (characterized by the chemical diffusivity D^δ). Depending on the material, the geometry of the sample and the temperature, the overall process can be determined by different steps. As pointed out by Otter et al., in ECR measurement, when the size of samples in one dimension is much less than the size of the other dimensions, one only needs to consider the smallest dimension in the direction of diffusion process [24]. In our work, the maximum ratio of thickness to the other two dimensions is 0.15, so the sample is in control of the thickness dimension. When sample much thinner than the critical thickness $L_{\text{crit}} = 2D/k$, the proton uptake process is exclusively surface exchange determined. Although initially are not known for hydrogenation of BCFZY, the effective thickness in this work, 0.35 mm should be much smaller than L_{crit} (which is always around 5–10 mm as reported for oxygen surface exchange relaxation [25]). And proton diffusion rate should be much faster than that of oxygen ion due to lower activation energy, thus further prove that the proton uptake reaction should attribute more to the surface exchange process.

So the kinetics in this work is controlled by the surface exchange rate (k -determined) and it is determinable through ECR method to fit the relaxation curve as shown in Fig. 2. The experimental result is fitted with the surface exchange coefficient k^δ in formula of $NC(t) = 1 - \exp(-\frac{k^\delta}{d}t)$, as the fitting line in Fig. 2. These curves can be well fitted with a single effective k^δ , which also proved the hypothesis that the proton uptake reaction is governed by surface exchange process in our sample, and the fitted values k^δ are shown in Fig. 2d. At 600 °C, the k^δ value for BCFZY is $1.08 \times 10^{-5} \text{ cms}^{-1}$. And in the temperature range of 500–650 °C, the k^δ value decrease with reduced temperature, and finally arrives $3.85 \times 10^{-6} \text{ cm}^{-1}$ at 500 °C.

To investigate the effect of oxygen partial pressure, the relaxation curve under $p\text{O}_2$ of 1%, 21% and 100% was measured at 650 °C as shown in Fig. 3. It could be seen that, the relaxation time is 20000, 10000, and 2000s, from 1% to 100% $p\text{O}_2$, respectively. So we can conclude that the time required for proton exchange reaction decreases with the increased $p\text{O}_2$, and the derived k^δ values are 6.83×10^{-6} , 1.52×10^{-5} and $7.69 \times 10^{-5} \text{ cms}^{-1}$. In the hydrogenation reaction as

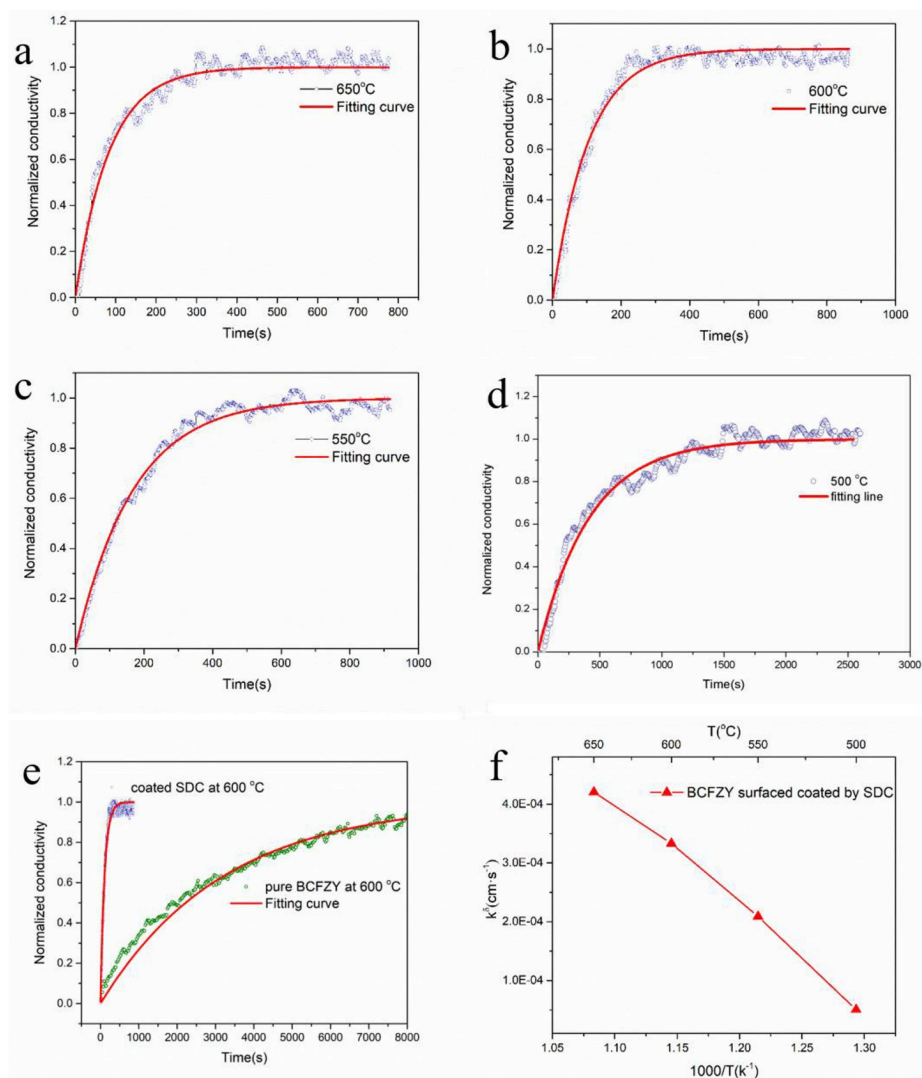


Fig. 4. (a–d) The normalized conductivity curve of BCFZY surfaced coated by SDC at 650, 600, 550 and 500 °C, (e) compare the relaxation between pure BCFZY and BCFZY coated with SDC and (f) the proton surface exchange coefficient k^δ of BCFZY after surface coated with SDC particles at different temperatures.

Eq.(2), hole as reactant is consumed in proton incorporation process, so hole concentration $[h^*]$ is the dominant factor for the reaction since the other factor are the same in the test condition. While for BCFZY as a P-type conductor, $[h^*]$ would be in a positive relationship with oxygen partial pressure as $[h^*] \propto [pO_2]^{1/4}$. So it means that the hole concentration $[h^*]$ in $pO_2 = 100\%$ is 3.16 times larger than that in $pO_2 = 1\%$, thus cause significantly higher proton uptake reaction rate. It is also reported by Poetzsch et al. [19] that the relaxation time of $Ba_{0.5}Sr_{0.5}Fe_{0.8}Zn_{0.2}O_{3-\delta}$ and $BaCo_{0.4}Fe_{0.4}Zr_{0.2}O_{3-\delta}$ show the same tradition under higher oxygen partial pressure as well as faster proton uptake kinetics.

3.3. Effect of SDC in proton uptake kinetic

Previous studies have reported that deposition of secondary phase like ionic conductors can significantly improve their oxygen surface exchange kinetics [26–28]. In our work, we determined the effect of SDC on proton uptake by depositing SDC on the surface of BCFZY sample. Surface SEM images of the BCFZY with and without SDC particles are shown in Fig. S1. It could be seen that BCFZY is wholly dense with the grain size of about 5 μm , and SDC particles are uniformly deposited on BCFZY surface which is pointed out in Figs. S1c–d.

The normalized conductivity curve of BCFZY sample with SDC particles modification on the surface from 650 to 500 °C were shown in

Fig. 4a–d. It is obvious that BCFZY spends more than 8000 s to reach equilibrium state at 600 °C, but it is reduced to about 400 s after BCFZY surface was coated with SDC, as shown in Fig. 4e. Since SDC particles are only deposited on the surface of BCFZY, and the protonic transport properties within BCFZY bulk should not be affected by the surface properties, so the proton diffusion process in bulk would not be changed. Therefore, the change in relaxation time of BCFZY with SDC could only be attributed to the proton surface exchange rate since the gas phase condition are kept the same. So a marketable enhancement of k^δ value is observed when SDC was coated on BCFZY surface. Fig. 4f shows the k^δ value of BCFZY coated with SDC at different temperatures. At 600 °C, the k^δ value can reach up to $3.33 \times 10^{-4} \text{ cm s}^{-1}$ which is one magnitude larger than that of pure BCFZY, $1.08 \times 10^{-5} \text{ cm s}^{-1}$. And the k^δ values are in the range of 10^{-4} to $10^{-5} \text{ cm s}^{-1}$ from 500 to 650 °C, which are much higher than that of pure BCFZY. The increase in proton surface exchange rate for BCFZY coated with SDC cannot be attributed to BCFZY surface since the effective surface area exposed to the gas phase should have been reduced. Therefore, the increase of k^δ values may be originated from the reaction occurring at the BCFZY-SDC interface where gas is available. Even Sun et al. [29] have reported that SDC has a very low proton conductivity of $3.03 \times 10^{-6} \text{ Scm}^{-1}$ at 950 °C measured by hydrogen permeation on supported SDC film, not mention the proton conductivity at 500–650 °C, which should be ever lower than that of

BCFZY, so the impressive enhancement effect could not be attributed to the proton directly transported from SDC. And due to the hydrogenation reaction that occurred at the expense of hole and lattice oxygen, the deposition of SDC on BCFZY surface is obviously could not contribute to the these.

4. Conclusions

The electrical conductivity relaxation method was used to measure the proton uptake process in proton/oxygen ion/hole triple conductor BCFZY by the change of water partial pressure under constant temperature and pO_2 . The proton uptake reaction was demonstrated to happen in hydrogenation with the sacrifice of holes for BCFZY at high oxygen partial pressure in this work. The proton surface exchange coefficient, k^{δ} , was derived from the relaxation curve, which is $1.08 \times 10^{-5} \text{ cm s}^{-1}$ for BCFZY at 600 °C. And it was found that higher oxygen partial pressure would accelerate the proton uptake kinetics due to higher hole concentration. And doped ceria was proved to could greatly accelerate the proton surface uptake process, thus improving the k^{δ} value to $3.33 \times 10^{-4} \text{ cm}^{-1}$ at 600 °C. Further studies are necessary to achieve insights into the proton uptake process and features that govern the enhancement role of SDC in BCFZY.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jpowsour.2019.227122>.

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