Taking advantage of Li-evaporation in LiCoO₂ as cathode for proton-conducting solid oxide fuel cells

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Abstract: LiCoO₂, a widely used electrode material for Li-ion batteries, was found to be suitable as a cathode material for proton-conducting solid oxide fuel cells (H-SOFCs). Although the evaporation of Li in LiCoO₂ was detrimental to the Li-ion battery performance, the Li-evaporation was found to be beneficial for the H-SOFCs. The partial evaporation of Li in the LiCoO₂ material preparation procedure led to the in-situ formation of the LiCoO₂+Co₃O₄ composite. Compared to the cell using the pure phase LiCoO₂ cathode that only generated moderate fuel cell performance, the H-SOFCs using the LiCoO₂+Co₃O₄ cathode showed a high fuel cell performance of 1160 mW·cm⁻² at 700 °C, suggesting that the formation of Co₃O₄ was critical for enhancing the performance of the LiCoO₂ cathode. The first-principles calculation gave insights into the performance improvements, indicating that the in-situ formation of Co₃O₄ due to the Li-evaporation in LiCoO₂ could dramatically decrease the formation energy of oxygen vacancies that is essential for the high cathode performance. The evaporation of Li in LiCoO₂, which is regarded as a drawback for the Li-ion batteries, is demonstrated to be advantageous for the H-SOFCs, offering new selections of cathode candidates for the H-SOFCs.

Keywords: cathode; composite; proton conductor; solid oxide fuel cells (SOFCs)

1 Introduction

The current energy and environmental problems require the development of sustainable technologies and devices [1–5], and solid oxide fuel cells (SOFCs) that can convert chemical energies into electricity receive considerable attention [6]. The traditional SOFCs have to work at high temperatures (above 800 °C), reducing the lifetime of the fuel cells [7,8]. Therefore, the development of the SOFCs working at lower temperatures (below 700 °C) is highly desirable, and proton-conducting SOFCs (H-SOFCs) are proposed [9–11]. The H-SOFCs are able to work at low temperatures due to the high conductivity and low activation energy of the proton-conducting electrolytes [12–15]. However, the low working temperatures also result in slow cathode kinetics, making the development of cathodes a hot and important topic [16,17].

In the past decades, different cathode materials have been proposed for the H-SOFCs [18,19]. Although some of these cathode materials give good performance, none of them have been made into practical applications yet. If one has a broader view and focuses not only on the materials for the H-SOFCs, the electrode materials for the Li-ion batteries and H-SOFCs share some

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common points. Many of these electrode materials are ceramic oxides and contain transition metals as their major compositions. Therefore, it would be reasonable to expect that some electrode materials for the Li-ion batteries could show decent performance for the H-SOFCs as well. More importantly, many of the electrode materials for the Li-ion batteries have been commercialized, and the application of the Li-ion battery electrode materials for the H-SOFCs could advance the development of the H-SOFCs.

In fact, some lithiated oxide cathodes have been used for the SOFCs, but only moderate performance has been achieved [20]. Very recently, LiCoO$_{0.6}$X$_{0.4}$O$_2$ ($X =$ Mn, Sr, and Zn) materials were applied as the cathodes for the H-SOFCs, and the optimal polarization resistance ($R_p$) is 0.55 $\Omega \cdot \text{cm}^2$ at 700 $^\circ\text{C}$ [21], which is inferior to the newly developed high-performing cathodes. These results imply that the traditional lithiated oxide cathodes might not be a good choice as the cathode candidate for the H-SOFCs. However, all of these have focused on using pure phase lithiated oxide cathodes and evaluated their suitability as the cathodes for the H-SOFCs. The lithiated oxide cathodes, such as the classical LiCoO$_2$, contain a large amount of Li element, and the Li element tends to evaporate during the synthesis procedure due to the high-temperature calcination. Therefore, an excess amount of Li should be added during the preparation process to compensate for the Li-evaporation and obtain the pure phase LiCoO$_2$ [22,23]. It is understandable that the Li loss could be detrimental to the performance of the Li-ion batteries, and the Li-evaporation has to be compensated [24]. However, the working mechanism of the H-SOFCs is different from that of the Li-ion batteries, which does not require the mobility of the Li-ions. It should be noted that the performance of the lithiated oxide cathodes for the H-SOFCs is reported to be only moderate [20,21], even though efforts are devoted to preparing the pure phase lithiated oxide cathodes. One may wonder about the performance of the lithiated oxide cathode for the H-SOFCs if the evaporated Li is not compensated, as no mobility of Li is needed in the H-SOFCs. Therefore, the classical Li-ion battery electrode LiCoO$_2$ was used in this study as the cathode for the H-SOFCs. The phase compositions for LiCoO$_2$ with and without the Li compensation were studied, and their performance for the H-SOFCs was investigated and compared, aiming to provide a new cathode system for the H-SOFCs.

2 Materials and method

LiCoO$_2$ was prepared by using Li$_2$CO$_3$ and Co(NO$_3$)$_3$ as starting materials [25]. Li$_2$CO$_3$ was dissolved in dilute nitric acid. According to Refs. [22,24], 4 mol% Li-excess was needed to compensate for the Li-evaporation during the synthesis to form the pure phase LiCoO$_2$. In contrast, the stoichiometric ratio of Li$_2$CO$_3$ and Co(CO$_3$)$_3$ was used in this study, making the molar ratio of Li : Co keep at 1 : 1 for the starting materials. In other words, no Li-excess was applied to compensate for the Li-evaporation during the synthesis procedure. The as-prepared powders were calcined at 850 $^\circ\text{C}$ for 3 h, followed by the phase examination using X-ray diffraction (XRD). The XRD was performed at a scanning rate of 3 ($^\circ$)·min$^{-1}$ with Cu K$_\alpha$ radiation. The morphologies of the powders were characterized by scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HR-TEM). The stability of the powders was examined by treating the powders in both CO$_2$ and H$_2$O-containing atmospheres at a high temperature. The CO$_2$ and H$_2$O concentrations were 20% and 30%, respectively. Then, the XRD was used to analyze the phase of the powders before and after the treatments.

To evaluate the efficiency of the LiCoO$_2$ cathodes for the H-SOFCs, the cathode slurry was deposited onto the electrolyte, and then being co-fired at 800 $^\circ\text{C}$ for 10 min. The electrolyte material used in this study was BaCe$_{0.7}$Zr$_{0.1}$Y$_{0.2}$O$_{3-\delta}$ (BCZY), and the anode was NiO–BCZY. The details for the preparations of the electrolyte powders and half-cells can be found in Ref. [26]. The single cells were tested by using humidified H$_2$ (3% H$_2$O) as the fuel. IV and electrochemical impedance spectroscopy (EIS) measurements were carried out by an electrochemical workstation (Squidstat Plus, Admiral Instrument) under open circuit voltage (OCV) condition. The frequency range was from 1 MHz to 0.1 Hz with an amplitude of 5 mV. The morphologies of the tested cells were observed by the SEM.

The first-principles calculation was carried out to investigate the LiCoO$_2$-based material, using density functional theory (DFT) method with Vienna Ab-initio Simulation Package (VASP) software. The calculation details can be found in Refs. [27–31].
3 Results and discussion

Figure 1(a) shows the XRD pattern for LiCoO$_2$ without Li-excess after being fired at 850 °C for 3 h. The LiCoO$_2$ powders with 4 mol% Li-excess were also prepared via the same procedure, and its XRD is shown in Fig. 1(a) as well. A pure phase is obtained with the LiCoO$_2$ powders with 4 mol% Li-excess. No other Li-related compounds, such as Li$_2$O or Li$_2$CO$_3$, can be detected. This result suggests that the excess Li compensates for the Li-evaporation during the calcination procedure, agreeing with Ref. [24] that 4 mol% Li-excess is usually used to offset the Li-evaporation during the synthesis process, making LiCoO$_2$ achieve a pure phase. In contrast, if one looks at the XRD pattern of the LiCoO$_2$ powders without Li-excess, the main peaks correspond to the LiCoO$_2$ phase. However, some extra peaks corresponding to Co$_3$O$_4$ can be found, suggesting that the evaporation of Li in LiCoO$_2$ could lead to Co$_3$O$_4$ as the second phase if the Li-evaporation is not compensated by excess Li sources. Figure 1(b) shows the SEM image of the LiCoO$_2$ powders without Li-excess, and one can see that large sheet-like powders are LiCoO$_2$, and the small particles are Co$_3$O$_4$. The TEM image of the powders (Fig. 1(c)) shows a similar result that LiCoO$_2$ and Co$_3$O$_4$ form the

![Figure 1](image_url)
composite. The HR-TEM image shown in Fig. 1(d) presents the LiCoO$_2$/Co$_3$O$_4$ interface, indicating the $d$-spacing value of 4.756 Å corresponding to the (003) plane of LiCoO$_2$ and the $d$-spacing value of 2.436 Å corresponding to the (311) plane of Co$_3$O$_4$. To further demonstrate the formation of Co$_3$O$_4$ nanoparticles, additional SEM images were taken for LiCoO$_2$+Co$_3$O$_4$ (prepared by the exsolution of Co$_3$O$_4$ from LiCoO$_2$), Co$_3$O$_4$, and pure phase LiCoO$_2$ for analyzing the morphologies of these powders, and the results are shown in Fig. S1 in the Electronic Supplementary Material (ESM). One can see that Co$_3$O$_4$ are small nanoparticles, while the pure phase LiCoO$_2$ is a sheet-like shape. It is evident that the LiCoO$_2$+Co$_3$O$_4$ composite is the sheet-like LiCoO$_2$ surrounded by small Co$_3$O$_4$ nanoparticles. In addition, the elemental analysis (Fig. S2 in the ESM) indicates that these small nanoparticles only contain Co and O elements, confirming the formation of Co$_3$O$_4$. The C element detected as a carbon tape was used in the SEM observations, and the Au element detected as Au sputtering was used to increase the conductivity of the samples. Therefore, it can be concluded that the LiCoO$_2$ powders without Li-excess finally becomes the LiCoO$_2$+Co$_3$O$_4$ composite powders. Figure 1(e) shows the scheme of the LiCoO$_2$ powder preparation. After the sol–gel procedure, the precursor was calcined at 850 °C for 3 h. When there is excess Li, the Li-evaporation can be compensated with the production of the pure phase LiCoO$_2$. In contrast, when the stoichiometric ratio of Li and Co is used, no Li-excess is used, and thus no compensation of the Li-evaporation happens for the final product, leading to the formation of the LiCoO$_2$+Co$_3$O$_4$ composite. The compensation of Li to obtain the pure phase LiCoO$_2$ is understandable for the Li-ion batteries as the Li ions are required to move during the charge and discharge processes for the Li-ion batteries, and the deficiency in the Li content could lead to the reduced capacity of the batteries [32]. However, the Li-evaporation and the formation of Co$_3$O$_4$ might promote the cathode performance in the fuel cells as Co$_3$O$_4$ is reported to facilitate the oxygen reduction reaction (ORR) at the cathode for the SOFCs and improve the cathode performance [33]. Therefore, it is reasonable to expect that the LiCoO$_2$+Co$_3$O$_4$ composite could give a good performance for the H-SOFCs.

Figure 2(a) shows the IV and power density curves of a single H-SOFCs using the LiCoO$_2$+Co$_3$O$_4$ composite as the cathode. The cell’s peak power densities (PPDs) are 1160, 896, and 603 mW·cm$^{-2}$ at 700, 650, and 600 °C, respectively. The PPDs tested at a temperature higher than 700 °C are not reported here, as obvious oxygen-ion conductions appear for proton-conducting oxides above 700 °C [4]. Figures 2(b)–2(d) show the cross-sectional view of the tested cell. A tri-layer structure can be observed, and the electrolyte layer contacts well with the cathode and anode. The fuel cell performance is much higher than those of the H-SOFCs using the traditional cathodes and comparable to or even higher than those of many recently developed cathodes, as indicated in Table 1 [34–42]. This result suggests that the LiCoO$_2$+Co$_3$O$_4$ composite is a high-performance cathode for the H-SOFCs.

The cell performance between the pure phase LiCoO$_2$ cathode and the LiCoO$_2$+Co$_3$O$_4$ cathode was further compared. Figure 3(a) shows the performance of the two cells using the LiCoO$_2$ cathode and the LiCoO$_2$+Co$_3$O$_4$ cathode at 700 °C. The PPD for the cell using the LiCoO$_2$ cathode is 879 mW·cm$^{-2}$, and the PPD value increases to 1160 mW·cm$^{-2}$ for the cell using the LiCoO$_2$+Co$_3$O$_4$ cathode under the same testing condition. The EIS analysis confirms that the $R_p$ for the pure phase LiCoO$_2$ cathode is 0.123 Ω·cm$^2$, and the $R_p$ value decreases to 0.043 Ω·cm$^2$ for the cell using the LiCoO$_2$+Co$_3$O$_4$ cathode under the same testing condition. The shrinkage in the $R_p$ is about 65% with the use of the LiCoO$_2$+Co$_3$O$_4$ cathode instead of the pure phase LiCoO$_2$ cathode. The $R_p$ for the LiCoO$_2$+Co$_3$O$_4$ cathode is even smaller than those for many recently reported cathodes for the H-SOFCs, as indicated in Table 1. It should be noted that only LiCoO$_2$ or LiCoO$_2$+Co$_3$O$_4$ was used as the cathode, and the LiCoO$_2$-based material was not mixed with the BCZY to form the composite cathode. The close $R_{\text{ohmic}}$ for both cells is expected because both cells are identically prepared except for the different cathodes used. In addition, the same Ni–BCZY anode is used for both cells, so the considerable gap in the $R_p$ should come from the cathode. The performance enhancement for the LiCoO$_2$+Co$_3$O$_4$ cathode is not only observed at 700 °C but also
Table 1 Comparison of performance of current LiCoO$_2$+Co$_3$O$_4$ cathode with other recently reported cathode materials for H-SOFCs

| Cell configuration | Electrolyte thickness ($\mu$m) | Cathode composition | PPD (mW·cm$^{-2}$) | $R_p$ (700 ℃) (Ω·cm$^2$) | Year | Ref. |
|--------------------|---------------------------------|---------------------|-------------------|--------------------------|------|------|
| Ni–BCSF/BCSF/F–BCSF | 15                              | Ba$_2$Sr$_1$Co$_{0.5}$Fe$_{0.5}$O$_{2.9}$ | 580   | 680                | 2018 | [34] |
| Ni–BCZY/BCZY/LSN    | 15                              | La$_1$Sr$_3$NiO$_4$  | 243   | 330                | 2018 | [35] |
| Ni–BCZY/BCZY/LSN    | 15                              | Nd(Ba$_0.4$Sr$_0.4$Ca$_0.2$)Co$_{1.6}$Fe$_{0.4}$O$_{5.1}$ | 217   | 301                | 2018 | [36] |
| Ni–BCZY/BCZY/LSN    | 25                              | Ca$_2$Co$_{0.5}$O$_{2.9}$ | 150   | 220                | 2019 | [37] |
| Ni–BCZY/BCZY/LSN    | 32                              | Ba$_2$Sr$_1$Ca$_{1.17}$Nd$_{0.02}$Co$_{0.9}$O$_{2.9}$ | 570   | 776                | 2020 | [38] |
| Ni–BCZY/BCZY/LSN    | 32                              | Sr$_2$Fe$_{1.5}$Mo$_{0.4}$Zr$_{0.1}$O$_{6.1}$ | —     | 630                | 2020 | [39] |
| Ni–BCZY/BCZY/LSN    | 12                              | Pr$_2$BaNiMnO$_{6.9}$ | 465   | 730                | 2021 | [40] |
| Ni–BCZY/BCZY/LSN    | 25                              | La$_1$Sr$_3$Co$_{0.5}$Fe$_{0.5}$O$_{2.9}$ | 219   | 348                | 2021 | [41] |
| Ni–BCZY/BCZY/LSN    | 12                              | LiCoO$_2$–Co$_3$O$_4$ | 603   | 896                | 2022 | This work |

Note: BCSF is BaCe$_0.8$Sm$_{0.2}$F$_{0.1}$O$_{2.85}$, LSN is La$_1$Sr$_3$NiO$_4$, BCZY5 is BaCe$_0.8$Zr$_{0.2}$Y$_{0.2}$O$_{3.5}$, BCZYYb is BaZr$_{0.1}$Ce$_{0.7}$Y$_{0.1}$Yb$_{0.1}$O$_{3.5}$, NSCCF is Nd(Ba$_0.4$Sr$_0.4$Ca$_0.2$)Co$_{1.6}$Fe$_{0.4}$O$_{5.1}$, CC is Ca$_2$Co$_{0.5}$O$_{2.9}$, BSSNC is Ba$_2$Sr$_1$Ca$_{1.17}$Nd$_{0.02}$Co$_{0.9}$O$_{2.9}$, SFMZ is Sr$_2$Fe$_{1.5}$Mo$_{0.4}$Zr$_{0.1}$O$_{6.1}$, LSCF is La$_1$Sr$_3$Co$_{0.5}$Fe$_{0.5}$O$_{2.9}$, and LCO is LiCoO$_2$.

detected at other testing temperatures. Figures 3(c) and 3(d) show the $R_{\text{ohmic}}$ and $R_p$ measured at different testing temperatures, respectively. It is found that the $R_{\text{ohmic}}$ is similar for both cells tested at different temperatures, but the $R_p$ shows apparent differences. As a result, the performance of the LiCoO$_2$+Co$_3$O$_4$ cathode cell is evidently higher than that of the cell using the pure phase LiCoO$_2$ cathode, as shown in Fig. 3(e). This result suggests that the difference in the $R_p$ rather than the $R_{\text{ohmic}}$ leads to a significant difference in the cell performance for the LiCoO$_2$+Co$_3$O$_4$ cell and the LiCoO$_2$ cell. The use of LiCoO$_2$+Co$_3$O$_4$ cathode significantly improves the cathode performance and the fuel cell performance. Although the evaporation of Li in LiCoO$_2$ is not desirable for the Li-ion batteries, the Li-evaporation in LiCoO$_2$ and the subsequently formed Co$_3$O$_4$ second phase benefit its application in the H-SOFCs, leading to higher fuel cell performance and lower $R_p$ compared with the pure phase LiCoO$_2$ electrode. Not only is the higher performance for the
Fig. 3 Comparison of (a) fuel cell performance and (b) EIS for the H-SOFCs using LiCoO$_2$+Co$_3$O$_4$ and LiCoO$_2$ cathodes tested at 700 °C; comparison of (c) $R_{\text{ohmic}}$, (d) $R_p$, and (e) PPDs for cells using LiCoO$_2$+Co$_3$O$_4$ and LiCoO$_2$ cathodes tested from 600 to 700 °C.

LiCoO$_2$+Co$_3$O$_4$ cathode compared with that for the pure phase LiCoO$_2$ cathode in this study, but also the $R_p$ of the current LiCoO$_2$+Co$_3$O$_4$ cathode is one or two orders of magnitude smaller than that of the lithiated oxide cathodes for the H-SOFCs reported in Ref. [21], which is 0.55 to a few $\Omega \cdot \text{cm}^2$ at 700 °C, even though the studies on the lithiated oxide cathodes for the H-SOFCs are very scarce. This result suggests that the in-situ formation of Co$_3$O$_4$ could dramatically improve the cathode performance and may bring a new life to the lithiated oxide cathodes for the H-SOFCs. It should be mentioned that further reducing the Li content does not further improve the cell performance. We have also synthesized the Li$_{0.95}$CoO$_2$ material, in which the Li content is further reduced, to check whether further reducing the Li content can further increase or decrease the cell performance. The fuel cell performance with the Li$_{0.95}$CoO$_2$ cathode is shown in Fig. S3 in the ESM. The cell’s PPDs are 1002, 657, and 422 mW·cm$^{-2}$ at 700, 650, and 600 °C, respectively. Although the performance is still larger than that of the fuel cell using the pure phase LiCoO$_2$, the performance is reduced compared with that of the LiCoO$_2$+Co$_3$O$_4$ composite reported above.

The DFT calculations were performed to give insights into the high performance of the LiCoO$_2$+Co$_3$O$_4$ cathode. The formation of oxygen vacancies ($V_O$) is critical for the cathode performance as it dramatically influences the ORR activity of the cathode [43] and the oxygen-ion diffusions [44]. The Li-evaporation could lead to the loss of Li$^+$, and extra oxygen vacancies are formed for the charge compensation. The defect reaction can be written as $2\text{Li}_{\text{Li}} \rightarrow 2\text{V}_{\text{L Li}}^\text{Li} + \text{V}_O^\text{Li}$, where $\text{V}_{\text{L Li}}^\text{Li}$ represents the Li vacancy due to the Li-evaporation, and $\text{V}_O^\text{Li}$ is the oxygen vacancy. In addition, the formation of $V_O$ is the pre-factor for the protonation according to the reaction $\text{H}_2\text{O} + \text{V}_O^\text{Li}^* + \text{O}_L \Leftrightarrow 2\text{OH}^*$, where $\text{O}_L$ means the lattice oxygen, and $\text{OH}^*$ means the proton defect, which is another crucial parameter for the cathode of H-SOFCs [45]. Therefore, the formation energies of $V_O$ ($E_{V_O}$) for the pure phase LiCoO$_2$ and LiCoO$_2$/Co$_3$O$_4$ are calculated. The $E_{V_O}$ was calculated according to

$$E_{V_O} = E_{\text{defect}} + \frac{1}{2}E_{O_2} - E_{\text{perfect}}$$

[29], where $E_{\text{defect}}$ is the total energy of defective bulk, $E_{O_2}$ is the energy of molecular oxygen, and $E_{\text{perfect}}$ is the total energy of the perfect bulk. The $E_{V_O}$ for LiCoO$_2$ is calculated to be 3.76 eV, which is relatively large compared with those for other cathode materials for the SOFCs. This result indicates that the $V_O$ formation in the pure phase LiCoO$_2$ has to overcome a high energy barrier. This result could explain that the reported lithiated oxide cathodes only show moderate performance for the SOFCs. When the LiCoO$_2$ material is prepared without an excess of Li, the final product is the LiCoO$_2$+Co$_3$O$_4$ composite, and Fig. 4(a) shows the DFT-calculated configuration of the LiCoO$_2$/Co$_3$O$_4$ supercell. Both the
bulks of LiCoO$_2$ and Co$_3$O$_4$ are calculated for structural optimizations. Then, the (104) surface of LiCoO$_2$ and the (110) surface of Co$_3$O$_4$ are cleaved for the combination. The (104) surface used for LiCoO$_2$ and the (110) surface used for Co$_3$O$_4$ are based on the previous reports as they are the most exposed surfaces for LiCoO$_2$ [46,47] and Co$_3$O$_4$ [48,49]. The supercell of the LiCoO$_2$ and Co$_3$O$_4$ surfaces are expanded to make a similar lattice constant between LiCoO$_2$ and Co$_3$O$_4$, and then the combination can be obtained. The final supercell for the LiCoO$_2$/Co$_3$O$_4$ contains 216 atoms. There are a certain number of LiCoO$_2$/Co$_3$O$_4$ interfaces. For the LiCoO$_2$/Co$_3$O$_4$ interface, we have performed the $E_{V_0}$ calculation at both LiCoO$_2$ and Co$_3$O$_4$ sides, and found that the $E_{V_0}$ at the LiCoO$_2$ side has the lowest energy, which means that the V$_O$ is more favourable to form at the LiCoO$_2$ side. The $E_{V_0}$ at the LiCoO$_2$/Co$_3$O$_4$ interface is calculated to be 0.46 eV, which is about one order of magnitude lower than that at the pure phase LiCoO$_2$, indicating that the V$_O$ formation is thermodynamically more favourable with the appearance of Co$_3$O$_4$. The oxygen species of LiCoO$_2$ and LiCoO$_2$+Co$_3$O$_4$ are investigated by X-ray photoelectron spectroscopy (XPS), and the results are shown in Figs. 4(b) and 4(c), respectively. The ratio between the adsorbed oxygen and the lattice oxygen reflects the V$_O$ content [50,51], and the ratio is 0.69 and 1.02 for LiCoO$_2$ and LiCoO$_2$+Co$_3$O$_4$, respectively, suggesting that the V$_O$ content in LiCoO$_2$+Co$_3$O$_4$ is higher than that in the pure phase LiCoO$_2$ that agrees with the DFT calculation results. The iodometric titration method was further used to measure the oxygen vacancy content in LiCoO$_2$ and LiCoO$_2$+Co$_3$O$_4$. It is found that the oxygen vacancy concentration in the pure phase LiCoO$_2$ is 0.13, and the value increases to 0.22 for the LiCoO$_2$+Co$_3$O$_4$ composite, suggesting an increase in the oxygen vacancies for LiCoO$_2$+Co$_3$O$_4$ compared with those for the pure phase LiCoO$_2$. The result is consistent with the DFT calculations and XPS analysis.

In addition, the distance between Co 3d and O 2p in LiCoO$_2$+Co$_3$O$_4$ is reduced compared with that in the pure phase LiCoO$_2$. Figures 5(a) and 5(b) show density of states (DOS) for Co 3d and O 2p orbitals for LiCoO$_2$ and LiCoO$_2$+Co$_3$O$_4$, respectively. The distance between Co 3d and O 2p is 3.17 for the pure phase LiCoO$_2$, and the value decreases to 2.86 with the appearance of Co$_3$O$_4$ for LiCoO$_2$+Co$_3$O$_4$. The reduced distance between Co 3d and O 2p is associated with enhanced charge transfer, thereby benefiting the ORR [52]. Therefore, the LiCoO$_2$+Co$_3$O$_4$ cathode performs better compared to the pure phase LiCoO$_2$. 

![Fig. 4](image-url) (a) DFT-calculated configuration for LiCoO$_2$/Co$_3$O$_4$ structure. XPS O 1s curves for (b) LiCoO$_2$ and (c) LiCoO$_2$+Co$_3$O$_4$.

![Fig. 5](image-url) DFT-calculated DOS of Co 3d and O 2p orbitals in (a) LiCoO$_2$ and (b) LiCoO$_2$+Co$_3$O$_4$, where $\epsilon_p$ means the p-band center for O 2p, and $\epsilon_d$ means the d-band center for Co 3d.
As the cathode for the H-SOFCs, another primary concern is the stability of the material, as this parameter is essential for its potential practical applications. The LiCoO$_2$+Co$_3$O$_4$ composite was treated in the CO$_2$-containing atmosphere at 600 °C, and the result is shown in Fig. 6(a). One can see that there is no extra peak under the treatment of 12 h, suggesting that the LiCoO$_2$+Co$_3$O$_4$ composite has good chemical stability against CO$_2$. The good chemical stability of the LiCoO$_2$+Co$_3$O$_4$ composite can be expected that no high-basicity element (such as Ba) is involved in the material, restricting its reaction with acid gases (such as CO$_2$). The LiCoO$_2$+Co$_3$O$_4$ composite also presents good chemical stability against steam. The composite powders were treated in a 30% H$_2$O-containing air atmosphere at 600 °C for 10 h. Figure 6(b) shows the XRD patterns for the LiCoO$_2$+Co$_3$O$_4$ composite before and after the treatment. The XRD pattern remains unchanged after the treatment, suggesting that there is no evident reaction between the LiCoO$_2$+Co$_3$O$_4$ composite and H$_2$O$_2$, thus demonstrating its excellent stability against H$_2$O at high temperatures. If we enlarge the XRD patterns before and after the treatment, one can see that the XRD peak slightly shifts to a lower angle after the treatment (Fig. S4 in the ESM), suggesting the expansion of the lattice. This phenomenon is also reported in Ref. [53], which is due to the adsorption of water in the lattice of the material. Although the peak shift is not very profound because the powders are treated at 600 °C, and the hydration degree decreases with the increasing temperatures [54], the peak shift can still be observed. The excellent chemical stability of the LiCoO$_2$+Co$_3$O$_4$ composite also leads to good fuel cell stability under the operation condition. Figure 6(c) shows the stability test result for the fuel cell. The cell works in a stable way for more than 500 h, suggesting that the LiCoO$_2$+Co$_3$O$_4$ composite provides high performance for the H-SOFCs and integrates the stability of the single-cell well.

4 Conclusions

In this study, we took advantage of the Li-evaporation in LiCoO$_2$ to form the LiCoO$_2$+Co$_3$O$_4$ composite as a cathode for the H-SOFCs. The Li-evaporation in LiCoO$_2$ was regarded as a drawback for the Li-ion batteries that required excess Li in the preparation procedure for the compensation. However, LiCoO$_2$ without the Li compensation turned out to be the LiCoO$_2$+Co$_3$O$_4$ composite after the calcination, which was applied as the cathode for the H-SOFCs. The LiCoO$_2$+Co$_3$O$_4$ composite generated higher fuel cell performance and lower $R_p$ for the H-SOFCs compared with the pure phase LiCoO$_2$ cathode. The DFT calculations coupled with experiments indicated that the appearance of Co$_3$O$_4$ due to the Li-evaporation in LiCoO$_2$ was beneficial to the formation of the oxygen vacancies, facilitating the cathode reactions. The improved oxygen vacancy content and the enhanced catalytic activity induced by the formation of the Co$_3$O$_4$ nanoparticles contribute to better cathode performance and larger fuel cell output. In addition, the high electrochemical performance of LiCoO$_2$+Co$_3$O$_4$ for the H-SOFCs did not impair its stability. The LiCoO$_2$+Co$_3$O$_4$ composite presented excellent stability in both CO$_2$ and H$_2$O. In addition, the good stability of the single-cell using the LiCoO$_2$+Co$_3$O$_4$ cathode under the working condition was also demonstrated, suggesting that LiCoO$_2$+Co$_3$O$_4$ composite integrated both high performance and good stability. This study bridges the electrode materials between the Li-ion batteries and the H-SOFCs and indicates that the disadvantageous feature in the Li-ion batteries may
become an advantage for the H-SOFCs, probably opening a new area of cathode design for the H-SOFCs.

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Declaration of competing interest

The authors have no competing interests to declare that are relevant to the content of this article.

Electronic Supplementary Material

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References

[1] Zhang YW, Mei J, Yan C, et al. Bioinspired 2D nanomaterials for sustainable applications. Adv Mater 2020, 32: 1902806.
[2] Sun ZQ, Liao T, Li WX, et al. Beyond seashells: Bioinspired 2D photonic and photoelectronic devices. Adv Funct Mater 2019, 29: 1901460.
[3] Dai HL, Yin YR, Li XM, et al. A new Sc-doped La_{0.5}Sr_{0.5}MnO_{3−δ} cathode allows high performance for proton-conducting solid oxide fuel cells. Sustain Mater Techno 2022, 32: e00409.
[4] Iwahara H. Oxide-ionic and protonic conductors based on perovskite-type oxides and their possible applications. Solid State Ionics 1992, 52: 99–104.
[5] Ling JR, Zhou YF, Xu WT, et al. Red-emitting YAG:Ce,Mn transparent ceramics for warm WLEDs application. J Adv Ceram 2020, 9: 45–54.
[6] Zhang Y, Chen B, Guan DQ, et al. Thermal-expansion offset for high-performance fuel cell cathodes. Nature 2021, 591: 246–251.
[7] Zhang Y, Knibbe R, Sunarso J, et al. Recent progress on advanced materials for solid-oxide fuel cells operating below 500 °C. Adv Mater 2017, 29: 1700132.
[8] Liang MZ, He F, Zhou C, et al. Nickel-doped BaCo_{0.8}Fe_{0.2}Zn_{0.1}Y_{0.1}O_{3−δ} as a new high-performance cathode for both oxygen-ion and proton-conducting fuel cells. Chem Eng J 2021, 420: 127717.
[9] Wu S, Xu X, Li XM, et al. High-performance proton-conducting solid oxide fuel cells using the first-generation Sr-doped LaMnO_{3} cathode tailored with Zn ions. Sci China Mater 2022, 65: 675–682.
[10] Zvonareva I, Fu XZ, Medvedev D, et al. Electrochemistry and energy conversion features of protonic ceramic cells with mixed ionic-electronic electrolytes. Energ Environ Sci 2022, 15: 439–465.
[11] Xie D, Li K, Yang J, et al. High-performance La_{0.9}(Ba_{0.5}Ca_{0.5})_{0.1}Co_{0.8}Fe_{0.2}O_{3−δ} cathode for proton-conducting solid oxide fuel cells. Int J Hydrogen Energ 2021, 46: 10007–10014.
[12] Chen M, Xie XB, Guo JH, et al. Space charge layer effect at the platinum anode/BaZr_{0.9}Y_{0.1}O_{3−δ} electrolyte interface in proton ceramic fuel cells. J Mater Chem A 2020, 8: 12566–12575.
[13] Chen M, Chen DC, Wang K, et al. Densification and electrical conducting behavior of BaZr_{0.9}Y_{0.1}O_{3−δ} proton conducting ceramics with NiO additive. J Alloys Compd 2019, 781: 857–865.
[14] Li J, Wang C, Wang XF, et al. Sintering aids for proton-conducting oxides—A double-edged sword? A mini review. Electrochem Commun 2020, 112: 106672.
[15] Tian HC, Li WY, Ma L, et al. Deconvolution of water-splitting on the triple-conducting Ruddlesden–Popper-phase anode for protonic ceramic electrolysis cells. ACS Appl Mater Interfaces 2020, 12: 49574–49585.
[16] Yin YR, Yu SF, Dai HL, et al. Triggering interfacial activity of the traditional La_{0.5}Sr_{0.5}MnO_{3} cathode with Co-doping for proton-conducting solid oxide fuel cells. J Mater Chem A 2022, 10: 1726–1734.
[17] Zhang LL, Yin YR, Xu YS, et al. Tailoring Sr_{2}Fe_{0.5}MnO_{3}−δ with Sc as a new single-phase cathode for proton-conducting solid oxide fuel cells. Sci China Mater 2022, 65: 1485–1494.
[18] Tarutin AP, Lyagavaeva JG, Medvedev DA, et al. Recent advances in layered La_{2}NiO_{4−δ} nickelates: Fundamentals and prospects of their applications in protonic ceramic fuel and electrolysis cells. J Mater Chem A 2021, 9: 154–195.
[19] Song YF, Chen YB, Wang W, et al. Self-assembled triple-conducting nanocomposite as a superior protonic ceramic fuel cell cathode. Joule 2019, 3: 2842–2853.
[20] Zhang L, Lan R, Krafi A, et al. Cost-effective solid oxide fuel cell prepared by single step co-press–firing process with lithiated NiO cathode. Electrochem Commun 2010, 12: 1589–1592.
[21] Yusoff WNAW, Somalu MR, Baharuddin NA, et al. Enhanced performance of lithiated cathode materials of LiCo_{0.5}X_{0.5}O_{2} (X = Mn, Sr, Zn) for proton-conducting solid oxide fuel cell applications. Int J Energ Res 2020, 44: 11783–11793.
[22] Predoana L, Jitianu A, Voicescu M, et al. Study of formation of LiCoO_{2} using a modified Pechini aqueous sol–gel process. J Sol–Gel Sci Techn 2015, 74: 406–418.
[23] Li L, Chen RJ, Zhang XX, et al. Preparation and electrochemical properties of re-synthesized LiCoO_{2} from spent lithium-ion batteries. Chinese Sci Bull 2012, 57: 4188–4194.
[24] Han SJ, Xia YG, Wei Z, et al. A comparative study on the oxidation state of lattice oxygen among Li_{1.14}Ni_{0.136}Co_{0.136}−δ Mn_{0.54}O_{2}, Li_{2}MnO_{3}, Li_{1.6}Ni_{0.2}Co_{0.8}Mn_{0.3}O_{2} and LiCoO_{2} for
the initial charge–discharge. J Mater Chem A 2015, 3: 11930–11939.

[25] Xu X, Bi L, Zhao XS. Highly-conductive proton-conducting electrolyte membranes with a low sintering temperature for solid oxide fuel cells. J Membrane Sci 2018, 558: 17–25.

[26] Xu X, Xu YS, Ma JM, et al. Tailoring electronic structure of perovskite cathode for proton-conducting solid oxide fuel cells with high performance. J Power Sources 2021, 489: 229486.

[27] Xu X, Wang HQ, Fronzi M, et al. Tailoring cations in a perovskite cathode for proton-conducting solid oxide fuel cells with high performance. J Mater Chem A 2019, 7: 20624–20632.

[28] Tao ZR, Xu X, Bi L. Density functional theory calculations for cathode materials of proton-conducting solid oxide fuel cells. Electrochim Acta 2020, 344: 136143.

[29] Munoz-Garcia AB, Tuccillo M, Pavone M. Computational fuel cells: A mini-review. Electrochem Commun 2021, 129: 107072.

[30] Yin YR, Dai HL, Yu SF, et al. Proton-conducting solid oxide cathodes for solid oxide fuel cells. J Mater Chem A 2017, 5: 11825–11833.

[31] Xu YS, Xu X, Bi L. A high-entropy spinel ceramic oxide as the cathode for proton-conducting solid oxide fuel cells. J Adv Ceram 2022, 11: 794–804.

[32] Mei J, Liao T, Liang J, et al. Toward promising cathode catalysts for nonliathium metal–oxygen batteries. Adv Energy Mater 2020, 10: 1901997.

[33] Zhang HZ, Yang WS. Highly efficient electrocatalysts for oxygen reduction reaction. Chem Commun 2007: 4215–4217.

[34] Xie Y, Shi N, Huan DM, et al. A stable and efficient cathode for fluorine-containing proton-conducting solid oxide fuel cells. ChemSusChem 2018, 11: 3423–3430.

[35] Yang SJ, Wen YB, Zhang JC, et al. Electrochemical performance and stability of cobalt-free Ln0.5Sr0.5FeO3-δ cathode with a nonmetal cation-doping strategy for high-performance proton-conducting solid oxide fuel cells. SustainMat 2022, https://doi.org/10.1002/sus2.79.

[36] Xu YS, Xu X, Bi L. A high-entropy spinel ceramic oxide as the cathode for proton-conducting solid oxide fuel cells. J Adv Ceram 2022, 11: 794–804.

[37] Zhang HZ, Yang WS. Highly efficient electrocatalysts for oxygen reduction reaction. Chem Commun 2007: 4215–4217.

[38] Xie Y, Shi N, Huan DM, et al. A stable and efficient cathode for fluorine-containing proton-conducting solid oxide fuel cells. ChemSusChem 2018, 11: 3423–3430.

[39] Yang SJ, Wen YB, Zhang JC, et al. Electrochemical performance and stability of cobalt-free Ln0.5Sr0.5FeO3-δ cathode with a nonmetal cation-doping strategy for high-performance proton-conducting solid oxide fuel cells. SustainMat 2022, https://doi.org/10.1002/sus2.79.

[40] Wang Q, Hou J, Fan Y, et al. Pr2BaNiMnOδ-δ double-layered Ruddlesden–Popper perovskite oxide as efficient cathode electrocatalysts for low temperature proton conducting solid oxide fuel cells. J Mater Chem A 2020, 8: 7704–7712.

[41] Cao D, Zhou MY, Yan XM, et al. High performance low-temperature tubular protonic ceramic fuel cells based on barium cerate–zirconate electrolyte. Electrochem Commun 2021, 125: 106986.

[42] Ling YH, Guo TM, Guo YY, et al. New two-layer Ruddlesden–Popper cathode materials for protonic ceramics fuel cells. J Adv Ceram 2021, 10: 1052–1060.

[43] Xie D, Ling A, Yan D, et al. A comparative study on the composite cathodes with proton conductor and oxygen ion conductor for proton-conducting solid oxide fuel cell. Electrochim Acta 2020, 344: 136143.
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