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Promotion of oxygen reduction and evolution by applying a nanoengineered hybrid catalyst on cobalt free electrodes for solid oxide cells

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A key requirement for the widespread commercialization of solid oxide cell (SOC) technology is to develop cost-effective oxygen electrodes with sufficiently high electro-catalytic activity and durability at intermediate temperatures (600–750 °C). Here we report a remarkable enhancement of electro-catalytic activity of cobalt-free (La0.5Sr0.5Co2O4−δ) (LSF) electrodes by applying a nanoengineered hybrid catalyst coating composed of nanoparticles of Ce0.5Gd0.5O2−δ (CGO) and Pr6O11 via co-infiltration. Different from the conventional infiltration with a precursor of metal nitrate, here a mixture solution of colloidal CGO nanocrystals and Pr(NO3)3 is used for infiltration to enable the desired nanoengineered architecture. The resulting hybrid-catalyst-coated LSF electrode exhibits a very low polarization resistance of 0.017 Ω cm2 at 750 °C, about one order of magnitude lower than that of bare LSF (0.197 Ω cm2). Furthermore, the Ni/yttria-stabilized zirconia (YSZ) fuel-electrode-supported cell with this hybrid-catalyst-coated LSF electrode displays excellent performance in both fuel-cell and electrolysis operations, while it also offers good durability tracked over 1000 h of fuel-cell operation. The unique catalytic activity of the hybrid-catalyst-coated LSF electrode is attributed to the combined effects of accelerating oxygen surface exchange kinetics by Pr6O11 and enhancing the available surface area by the nanoporous architecture of the catalyst coating. Moreover, combining with the modification of the Ni/YSZ electrode, stable electrolysis operation at 650 °C under -0.5 A cm−2 with a voltage close to 1.3 V is achieved on a cell prepared without cobalt. This work not only opens the opportunity for applying cobalt-free oxygen electrodes in SOCs but also proposes a co-infiltration strategy to develop highly active and robust catalyst coating by combined tuning of composition and morphology, which may also be applicable to other devices such as metal-air batteries and membrane reactors.

1. Introduction

Owing to the rapid growth in electricity generation from intermittent renewable solar and wind sources, grid-scale and long-term (e.g., seasonal) energy storage is needed to balance the supply-demand mismatch.1–3 As a promising technology to address this energy storage challenge, solid oxide cells (SOCs) have received increasing attention in recent years.4–6 They can be operated either in electrolysis mode (as solid oxide electrolysis cells, SOECs) to convert H2O and/or CO2 into H2 and/or CO using excess renewable electricity, or in fuel-cell mode (as solid oxide fuel cells, SOFC) to generate electricity on demand using the fuels produced.5,7

Reducing the operating temperature to the intermediate temperature range (600–750 °C) will be highly beneficial for widespread commercialization of the SOC technology. One of the technical challenges for operating SOCs in this temperature range is to ensure sufficiently high electro-catalytic activity for the oxygen reduction reaction (ORR, when operated in fuel-cell mode) and the oxygen evolution reaction (OER, when operated in electrolysis mode) as well as good durability. During the past decades, substantial efforts have been made, leading to a shift in oxygen electrode materials from the conventional electronic conducting La0.8Sr0.2MnO3 (LSM) compound to mixed ionic-electronic conductors (MIECs). In particular, many cobalt-containing perovskite-type oxides, such as La0.8Sr0.2Co0.8Fe0.2O3−δ (LSCF)8,9, La0.5Sr0.5CoO3−δ (LSC)10, Ba0.5Sr0.5Co0.9Fe0.1O3−δ (BSFC)11,12, Sm0.5Sr0.5CoO3−δ (SSC)13, and PrBa0.8Ca0.2Co2O5+δ (PBCC)14 have been developed, and have shown to provide favorable catalytic activity at intermediate temperatures. Nevertheless, these cobalt-containing materials are not without problems. The materials show a large thermal expansion mismatch with commonly used electrolyte materials, i.e., yttria-stabilized zirconia (YSZ) and scandia-stabilized zirconia (SSZ). Their chemical stability is limited, which together with the volatilization and diffusion of cobalt during high-temperature sintering cause various cell fabrication issues.15–17 Furthermore, cobalt is price volatile and it may become resource-limited due to the rocketing demand of cobalt oxide for lithium-ion batteries.16 Finally, it is considered carcinogenic. All these factors push the development of cobalt-free electrodes for SOCs.

LaFeO3-based oxides are attractive alternatives because of their similar thermal expansion coefficients to that of the conventional electrolyte materials and improved chemical stability. Fe is highly abundant and low cost.18,19 However, LaFeO3-based materials exhibit relatively low catalytic activity for ORR and OER in comparison with cobalt-containing materials. For example, La0.5Sr0.5FeO3−δ electrode was reported to show a polarization resistance (RP) of 0.79 Ω cm2 at 700 °C, more than 2 times that of the most commonly used LSCF electrode (0.34 Ω cm2) and even ~11 times that of more cobalt-rich composite like PBCC electrodes (0.071 Ω cm2) under the same conditions. Recently, surface modification via infiltration of oxygen electrodes with catalytically-active nanoparticles/coating has emerged as an effective approach to enhance the activity.14,21–23 Those nanoparticles/coatings are generally introduced by infiltration of nitrate solutions that subsequently decomposed via heat treatment. By this approach the overall composition of the coating is well controlled but the
phase and the morphology of coating, which is also important for performance, is not well controlled.

Here, we report on (La0.6Sr0.4)0.98FeO3–δ (LSF)-based electrodes that can be strongly improved to a level allowing operation at ≥650 °C by applying a nanoengineered hybrid catalyst coating realized through a nonconventional infiltration route. The hybrid coating is composed of a nanoporous layer of nanoparticles of Ce0.8Gd0.2O2−δ (CGO) and Pr6O11. The coating is achieved by infiltrating the porous LSF backbone with a solution of colloidal CGO nanocrystals and Pr(NO3)3. Pr-oxide was included because of its good catalytic activity towards the ORR.21, 24, 25 The resulting hybrid-catalyst coated LSF electrode displayed a very low Rs of 0.017 Ω cm2 at 750 °C. This performance is superior to those of the cobalt-containing electrodes mentioned previously. The effect of coating on oxygen surface exchange kinetics was investigated by examining the distribution of relaxation time (DRT) of the impedance spectra and electrical conductivity relaxation (ECR) measurements. Moreover, the hybrid-catalyst-coated LSF electrode demonstrated excellent performance and durability in full cells for both practical fuel-cell and electrolysis operations.

2. Experimental

2.1 Synthesis and characterization of CGO nanocrystals

The CGO nanocrystals used in this work were synthesized by a continuous hydrothermal flow synthesis (CHFS) method. The process details can be found elsewhere.26 Shortly, in an in-house developed CHFS flow-type reactor, a precursor stream of Ce(NO3)3 (0.04 mol L−1) and Gd(NO3)3 (0.01 mol L−1) was mixed with a stream of supercritical water (396 °C, 26 MPa). The nanocrystals nucleated and grew upon mixing. The nanocrystals were collected in the outflow that was cooled down and depressurized to atmospheric pressure. The nanocrystals were then separated from the suspension by using a centrifuge, washed in deionized water and ethanol, and dried for later processes. Bright field TEM (BF-TEM) and high-resolution TEM (HR-TEM) images were taken on a JEOL 3000F field emission transmission electron microscope that operates at 300 kV.

2.2 Fabrication of symmetrical cells

Symmetrical cells with the bare LSF electrodes were prepared by printing an in-house developed LSF ink onto both sides of commercially available Ce0.8Gd0.2O2−δ (CGO10) electrolyte (KERAFL). The ink was obtained by mixing LSF powders (KUSAKA, 85 wt.%) and carbon powders (15 wt.%) in an organic vehicle composed of solvent, dispersant, and binder. After printing and drying, the cells were sintered at 1100 °C for 5 h to form porous LSF electrodes (with an active area of 0.28 cm2). Three types of symmetrical cells with CGO, Pr6O11, and the hybrid-catalyst (CGO+Pr6O11)-coated LSF electrodes, respectively, were prepared by infiltrating colloidal CGO solution, Pr(NO3)3 solution, and a mixture solution of colloidal CGO nanocrystals and Pr(NO3)3, into porous LSF backbones with subsequent calcination at 350 °C. Colloidal CGO was prepared by ultrasonically dispersing as-synthesized CGO nanocrystals in ethanol with polyethylene glycol (1 wt.%) as surfactant.27

2.3 Fabrication of fuel-electrode-supported cells

The fuel-electrode-supported half cells with a configuration NiO/YSZ support | NiO/YSZ fuel electrode | YSZ electrolyte | CGO10 barrier were produced by laminating and co-sintering tape-cast green tapes, as previously reported.28 The hybrid-catalyst-coated LSfnanocrystal oxygen electrode (with an area of 4 cm2) was then applied to the CGO barrier using the same procedures as described previously for the preparation of symmetrical cells. The modification of Ni/YSZ fuel electrode with CGO electrocatalysts was performed by a pre-reduction procedure followed by the infiltration of Ce0.8Gd0.2O2−δ (CGO20) nitrate precursor solution containing stoichiometric amounts of Ce(NO3)3 and Gd(NO3)3 (4:1 molar ratio to metal ions), as previously reported.29 The infiltration processes were repeated 7 times to get a loading of ~110 mg CGO20 per 1 cm3 Ni/YSZ structure (Ni/YSZ fuel electrode + Ni/YSZ support).

2.4 Electrochemical characterization

The electrochemical performance of bare/coated LSF electrodes was assessed on symmetrical cells at 650–750 °C in air. The setup used for the symmetrical cell measurements can
be found described elsewhere. The cells were heated to 750 °C with a heating rate of 1 °C min⁻¹ and held for 4 h during the start-up. The electrochemical performance and durability of the fuel-electrode-supported cells were investigated both in fuel-cell and electrolysis modes using in-house constructed test rigs. In fuel-cell mode, the cells were tested with 4%H₂O-96%H₂ fed to the fuel electrode and dry air to the oxygen electrode. In electrolysis mode, the cells were tested with 50%H₂O-50%H₂ fed to the fuel electrode and dry air to the oxygen electrode. Electrochemical impedance spectroscopy (EIS) measurements were conducted using a Solartron 1255 frequency response analyzer in combination with a measurement resistor, at frequencies from 0.1 to 10 kHz with an amplitude of 3.75 mA cm⁻². All of EIS data analyses were carried out using the Python-based software Ravdav.

The surface exchange kinetics of bare and catalyst-coated LSF were evaluated by electrical conductivity relaxation (ECR) measurement. Dense LSF bars were prepared by pressing, sintering, and polishing, as described in previous work. Surface coated LSF bars were prepared by a similar infiltration procedure as described above for three cells. The electrical conductivity was measured by the four-probe technique. The samples were heated to 750 °C with heating rate of 2 °C min⁻¹ and held for 4 h to calcine the coating. All the measurements were performed by changing pO₂ from 0.2 to 0.1 bar (reduction runs) and from 0.1 to 0.2 bar (oxidation runs). A detailed description of ECR measurement and data fitting can be found in our previous work.

3. Results and discussion
3.1 Microstructure of LSF electrodes

The shapes and exposed facets of the CGO nanocrystals were examined using TEM. Fig. 1a shows that CGO nanocrystals have well-defined octahedral shapes with sizes between 25-45 nm and mainly expose (111) facets with the lattice fringes at 0.31 nm. Shown in Fig. 1b is a typical SEM image of the bare LSF electrode backbone after firing at 1100°C for 5 h, showing smooth surfaces and clear grains. In Fig. 1c-e, images of CGO, Pr₆O₁₁, and the hybrid-catalyst (CGO+Pr₆O₁₁)-coated LSF electrodes after calcining at 750 °C for 4 h are displayed. Fig. 1c shows that CGO nanocrystals are uniformly deposited on the LSF grains and that they have maintained their shapes. Once coated with the Pr₆O₁₁ catalyst, a continuous and seemingly dense film is observed on the surface of the LSF grains, appearing rougher (Fig. 1d). Fig. 1e shows that the hybrid catalyst covers the LSF very well with particle size of 25–60 nm and forms a nanoporous coating. Compared to the dense Pr₆O₁₁ coating obtained after Pr(NO₃)₃ infiltration, this nanoporous hybrid catalyst coating achieved by co-infiltration of colloidal CGO nanocrystals and Pr(NO₃)₃ may largely enhance the available surface area for the catalytic reaction. This was demonstrated by the Brunauer - Emmett - Teller (BET) results, where surface areas for the bare LSF, CGO-coated LSF, Pr₆O₁₁-coated LSF, and hybrid-catalyst-coated LSF electrodes were found to be 1.2, 2.9, 2.1 and 3.0 m² g⁻¹, respectively. Introducing CGO nanocrystals may decrease the amount of praseodymium used which will reduce overall cost. Formation of the targeted CGO, Pr₆O₁₁ and CGO+Pr₆O₁₁ composite in the coatings is confirmed by the XRD patterns of powders, synthesized by calcinating the infiltrate solution at 750 °C (Fig. 1f). The phase reaction between LSF and as-coated CGO and Pr₆O₁₁ is considered negligible, based on our recent work and the previously reported results.
The electrochemical performance of the bare LSF, CGO-coated LSF, Pr$_6$O$_{11}$-coated LSF, and hybrid-catalyst-coated LSF electrodes was evaluated in symmetrical cells with a configuration of electrode/electrolyte/electrode. Fig. 2a and 2b compares Nyquist plots of the EIS data for the four types of electrodes obtained at 750 and 650 °C, respectively. All of the coated LSF electrodes show significantly reduced polarization resistances ($R_p$) when compared to the bare LSF. The hybrid-catalyst-coated LSF electrode displays the lowest $R_p$ among the four. For instance, the $R_p$ value of the hybrid-catalyst-coated LSF at 750 °C is 0.017 Ω cm$^2$, about one order of magnitude lower than that of the bare LSF (0.197 Ω cm$^2$), ~80% lower than that of CGO-coated LSF (0.089 Ω cm$^2$), and ~40% lower than that of Pr$_6$O$_{11}$-coated LSF (0.028 Ω cm$^2$) under the same conditions.

The here prepared hybrid-catalyst-coated LSF electrode is among the fastest ones reported on cobalt-free materials. Even though it is LSF based and cobalt-free, its performance matches those of the high-performance cobalt-containing electrodes reported recently, including LSCF or LSCF nanofiber, BSCF-CGO mixture or nanofibers, SrTi$_{0.3}$Fe$_{0.63}$Co$_{0.07}$O$_{3-\delta}$ (STFC-07) and PBCC$^{37}$ as well as several representative surface-coated-electrodes such as Pr$_{0.4}$Sr$_{0.6}$CoO$_{2.8}$ (PSCM)-coated LSCF$^{38}$, multi-phase catalysts (composed of BaCoO$_{3-x}$ (BCO) and PrCoO$_{3-x}$ (PCO) nanoparticles and a conformal PBCC thin film)-coated LSCF$^{39}$, SSC-coated LSCF/CGO$^{10}$, PrNi$_{0.5}$Mn$_{0.5}$O$_3$ (PNM) thin film and PrO$_x$ nanoparticles-coated LSCF$^{21}$, and cobaltite-coated PBCC$^{41}$ (Fig. 2c). Even faster Pr-oxide-coated electrodes have been reported on CGO$^{10}$ backbone (Rp of 0.028 Ω cm$^2$ at 600 °C) and LaNi$_{0.6}$Fe$_{0.4}$O$_{3-\delta}$ (LNF)/CGO$^{10}$ composite backbone ($R_p$ of 0.074 Ω cm$^2$ at 650 °C)$^{35}$, but they were prepared with much higher Pr-oxide loadings of ~30 wt.% relative to the backbones and lower calcination temperatures of 600 °C. The higher loading and lower calcination temperature can indeed benefit the electrode performance, but the higher loading also means higher costs and the lower calcination temperature such as 600 °C aforementioned may render the electrodes susceptible to degradation by coarsening if stack initiation or operation takes place at higher temperature. It may be possible to improve the performance of the hybrid-catalyst-coated LSF electrodes further by, for example, using CGO nanocrystals with smaller sizes or optimizing the component ratio or loading of the hybrid catalyst. Such studies will be part of our future work.

The kinetics of the electrochemical processes on these LSF electrodes were investigated by examining the distribution of relaxation time (DRT) of the EIS data. DRT analysis is a useful tool for deconvoluting the complex EIS data to separate the contributions of some key steps from the total $R_p$ of the electrode reaction.$^{42, 43}$ In general, each peak in the DRT plot represents an electrode process, and its integral area corresponds to the resistance contribution of that process. The higher the characteristic frequency of the peak, the faster the relaxation of the corresponding process. Shown in Fig. 2d is the comparison of DRT plots for symmetrical cells with the four electrode conditions at OCV. Fig. 2e and 2f shows the durability on symmetrical cells with four types of LSF electrodes at 700 °C under OCV condition. (f) DRT plots at 0 h and 120 h.

oxide-coated electrodes have been reported on CGO10
types of LSF electrodes. Fig. S1 contains Nyquist and DRT plots of bare LSF electrode under different oxygen partial pressures (pO\textsubscript{2}) and of the hybrid-catalyst-coated electrode at different temperatures. In these DRT plots three distinct peaks are identified in the frequency range of 0.3–100 kHz, they are denoted as low frequency (LF), intermediate frequency (IF), and high frequency (HF). The LF peak has little dependence on temperature while the other peaks are characterized by a pronounced thermal activation (Fig. S1b). This strongly indicates that the LF peak is related to gas diffusion within the pores of the electrodes since gas diffusion is only mildly temperature dependent.\textsuperscript{39} The IF peak has a strong dependence on temperature and pO\textsubscript{2} (Fig. S1b and S1d), indicating that the IF peak is associated with the oxygen surface exchange processes including oxygen adsorption/desorption, dissociation, and/or surface diffusion.\textsuperscript{14, 39} The insensitivity of the HF peak to pO\textsubscript{2} (Fig. S1d) suggests that the HF peak is likely related to transport of O\textsuperscript{2-} within the LSF backbone and/or across the electrode/electrolyte interface, which are processes less dependent on pO\textsubscript{2}.\textsuperscript{14, 39} It is clearly seen in Fig. 2d that at 750 °C the resistance of the IF peak (surface exchange processes) dominates the total R\textsubscript{p} of the bare LSF electrode, and that this peak decreases significantly by introducing coatings on the electrode. Also, its characteristic frequency shifts to higher values. The hybrid-catalyst-coated electrode has the highest characteristic frequency and the lowest resistance of the IF peak. These results are consistent with results of characterizations of the surface exchange coefficient (k) from ECR measurements. The k value of a bar of LSF is significantly increased after coating with catalysts, and the hybrid catalyst coated LSF possesses the highest k value (Fig. S2). For example, the k values at 750 °C are 2.07 × 10\textsuperscript{-4}, 9.71 × 10\textsuperscript{-4}, 1.67 × 10\textsuperscript{-3} cm s\textsuperscript{-1} for the bare LSF, Pr\textsubscript{6}O\textsubscript{11}-coated LSF, and the hybrid-catalyst-coated LSF, respectively. The hybrid-catalyst-coated LSF electrode shows the highest k in ECR and lowest R\textsubscript{p} in the symmetrical cell due most likely to its unique nanostructure, which combines the effects of high intrinsic activity of Pr\textsubscript{6}O\textsubscript{11} and the large surface area enabled by the CGO nanocrystals, as shown in Fig. 3.

The short-term durability of the four types of LSF electrodes was investigated using symmetrical cells aged at 700 °C. The evolution of R\textsubscript{p} with time is summarized in Fig. 2e. The order in degradation rate is: bare LSF (0.49 mΩ cm\textsuperscript{2} h\textsuperscript{-1}) > Pr\textsubscript{6}O\textsubscript{11}-LSF > CGO-LSF > hybrid-LSF.
(0.14 mΩ cm² h⁻¹). Fig. 2f shows a comparison of DRT plots at 0 h and 120 h for the four types of symmetrical cells. After 120 h of tests, all of the DRT plots display a shift in characteristic frequency to lower frequency on the IF peak and an accompanying increase of the corresponding integral resistance, reflecting a reduced rate of the surface exchange process on the electrodes. Remarkably, the CGO-coated LSF and hybrid-catalyst-coated LSF electrodes show a significantly smaller increase in the IF peak resistance in comparison with that of Pr₆O₁₁-coated LSF, revealing a positive effect on electrode durability of introducing CGO nanocrystals into the coating.

3.3 Performance and durability of full cells incorporating the hybrid-catalyst-coated LSF oxygen electrodes

To evaluate the performance of the hybrid-catalyst-coated LSF oxygen electrode in an actual full cell, fuel-electrode-supported cells with a configuration of Ni/YSZ support | Ni/YSZ fuel electrode | YSZ electrolyte | CGO10 barrier | hybrid-catalyst-coated LSF oxygen electrode were fabricated and tested under both fuel-cell and electrolysis operating conditions (Fig. 4a). A cross-sectional view of the cell components is shown in Fig. S3. Fig. 4b shows the typical I-V-P curves of the cell tested under representative fuel cell conditions with 4%H₂O-96%H₂ fed to the fuel electrode and dry air to the oxygen electrode. For comparison, the performance of a cell with a bare LSF electrode (LSF cell) was also characterized under identical test conditions. The hybrid-catalyst-coated LSF cell delivers peak power densities (PPDs) of 1.57, 1.15, 0.67 W cm⁻² at 750, 700, and 650 °C, respectively, about 70, 130, and 170 % higher than those of the LSF cell (0.86, 0.44, 0.20 W cm⁻²). A similar accelerated degradation phenomenon has been observed in our previous work, where the cell degraded at rates of 0.066 V kh⁻¹ in the first 500 h and 0.162 V kh⁻¹ in the following 500 h. The EIS data shows that the Rₓₑᵣₓ is stable during the continuous electrolysis operation (Fig. 5d and 5e), whereas an increase in Rₓₑᵣₓ from 0.387 to 0.741 Ω cm² is observed.

In order to clarify the contributions of each electrode to the increase in Rₓₑᵣₓ the EIS data shown in Fig. 5e were analyzed using DRT. The results are shown in Fig. 5f. Fig. S5 presents the EIS data of the cell measured under different temperatures and gas conditions and corresponding DRT results. In all DRT plots four distinct peaks are identified, denoted P1 to P4 from high to low frequency, corresponding to at least four electrode processes. It is shown in Fig. S5b that the processes associated with P1, P2, and P3 are characterized by a pronounced thermal activation while P4 is not sensitive to temperature. Fig. S5d shows that P2 and P4 are very sensitive to the ratio of H₂O to H₂ in the fuel electrode while P1 and P3 are almost independent of that. On the basis of these results and previously reported analyses, P1 is likely related to the transport of oxygen anions through the ionic conducting networks in the electrodes, and the major contribution of P1 likely originates from the YSZ network of the fuel electrode; P2 is associated with the hydrogen evolution reaction (HER) at the triple-phase boundaries (TPBs) of the fuel-electrode; P3 is likely related to the OER at the active sites of the oxygen electrode and P4 represents the gas diffusion and conversion. Fig. 5f shows that among four peaks the integral resistance of P2 dominates the total Rₓₑᵣₓ initially (0 h) and has the activation energy of Rₓₑᵣₓ compared with the LSF cell (Fig. 4e), consistent with the more significant improvement in performance at low temperature observed from the I-V curves in Fig. 4a and 4b. Besides, a moderate reduction in the ohmic resistance (Rₒₑᵣₓ) was observed after the hybrid-catalyst coating. This could be attributed to the infiltration of Pr₆O₁₁ into the porous CGO10 barrier layer (Fig. S4) enabling increased electrical conductivity and also the improved electrical contact at the barrier-layer-electrode interface.40

Durability is one of the key factors determining the practical application of SOCs. The long-term durability of the hybrid-catalyst-coated LSF cell was evaluated at 650 °C in both fuel-cell and electrolysis modes, as shown in Fig. 5. When operated in fuel-cell mode under a constant current density of 0.5 A cm⁻², the cell experiences an initial degradation followed by an activation during the first 300 h (Fig. 5a). Subsequently, it displays excellent durability in the following 800 h. EIS data obtained during the durability test shows that it is the Rₓₑᵣₓ that dictates the evolution of total resistance (Fig. 5b). Rₓₑᵣₓ first increases and then decreases over the first 300 h, and stabilizes afterwards. Rₓₑᵣₓ is practically unaltered over the test period. The long-term durability of the hybrid-catalyst-coated LSF cell reported here competes well with those well performing cells.
largest increase over 500 h of operation. The increase in P2 is also accelerated from 200 h, corresponding well to the trend observed in Fig. 5c. This trend likely depends on the progress of microstructural evolution at the Ni/YSZ electrode, which is driven by the cell overpotential. The accelerated degradation is probably due to the fact that the accumulated microstructural damage and increased overpotential lead to additional and even worse microstructural damages, such as reduction of YSZ observable only at high overpotential.49 Further experiments are needed in order to clarify the different stages of degradation and the mechanisms behind. Noteworthy, the resistance of P3 is much smaller than that of P2 and remains relatively constant. These results suggest that the hybrid-catalyst-coated LSF oxygen electrode has good activity and durability for the OER when operated under these conditions, and among the two electrodes of the present cell, the Ni/YSZ fuel electrode is the one limiting cell performance and durability.

3.4 Performance and durability of double-side modified cell

The observed degradation of the Ni/YSZ fuel electrode during electrolysis operation is not surprising and has been reported previously.49-52 A Ni/YSZ electrode is degraded much faster in electrolysis mode than in fuel cell mode when operated at the same current density.53 Recently, encouraging progress has been made in understanding the degradation mechanism and in strategies to reduce degradation.29, 45, 46, 54, 55 We have found that surface modification of the Ni/YSZ electrode by coating nano-sized Ce0.8Gd0.2O2-δ (CGO20) electrocatalysts is an effective approach to enhance the cell durability.29, 45, 56 Here, we applied this approach to the hybrid-catalyst-coated LSF cell thus resulting in a double-side modified cell (with a CGO20-coated Ni/YSZ fuel electrode and the hybrid-catalyst-coated LSF oxygen electrode). At 1.3 V, the current densities of the such cell are 1.86, 1.41, 0.82 A cm⁻² at 750, 700, and 650 °C, respectively (Fig. 6a). These values are higher than those of the hybrid-catalyst-coated LSF cell under identical conditions (Fig. 4c), indicating (as expected) an improvement in cell performance by introducing CGO20 coating into the Ni/YSZ electrode. Fig. 6b shows the EIS data of the double-side modified cell at different temperatures. The corresponding R_p and R_ohm values are summarized in Fig. S6. It is worth noting that in this temperature range the R_ohm is higher than R_p and constitutes more than 50% of the total resistance. Accordingly, future efforts in improving cell performance should be devoted to reducing the R_ohm.

More importantly, the double-side modified cell shows a significantly enhanced long-term durability under an electrolysis current density of 0.5 A cm⁻² at 650 °C (Fig. 6c and 5d). After some degradation over the first 250 h, the degradation rate of the cell decreases continuously in the subsequent period. After 1400 h operation, the cell reached a voltage of 1.306 V (compared to 1.491 V after 500 h for the hybrid-catalyst-coated LSF cell) and a degradation rate of ~0.009 V kh⁻¹ (~0.69 % kh⁻¹). The EIS results shown in Fig. 6d reveals that R_ohm is almost constant over the entire test period and the increase of R_p is slowing down gradually, showing an

![Fig. 5 Durability on Ni/YSZ fuel-electrode-supported cells with the hybrid modified LSF oxygen electrode. Fuel-cell operation under a constant current density of 0.5 A cm⁻² at 650 °C with 4%H₂O-96%H₂ fed to the fuel electrode and dry air to the oxygen electrode. (a) Evolution of cell voltage and power density. (b) Evolution of R_ohm and R_p. Electrolysis operation under a constant current density of -0.5 A cm⁻² at 650 °C with 50%H₂O-50%H₂ fed to the fuel electrode and dry air to the oxygen electrode. (c) Evolution of cell voltage. (d) Evolution of R_ohm and R_p. (e) Nyquist plots and (f) DRT plots of EIS data recorded during electrolysis operation. The periodic fluctuation of cell voltage in Fig. 5a and 5c is due to recording EIS data.

**Figure 5**

- **SOFC**
  - Power density vs. time (a)
  - Cell voltage vs. time (a)
- **SOEC**
  - Power density vs. time (b)
  - Cell voltage vs. time (b)
- **EIS**
  - Nyquist plots (c)
  - DRT plots (d)
  - Resistance vs. time (e)
  - Power density vs. time (f)
increase in $R_p$ of less than 0.001 $\Omega \cdot cm^2$ for the last 500 h. Fig. 6e- 
g shows SEM images of the double-side modified cell after the durability test. No obvious growth of nanoparticles of hybrid 
catalyst in the oxygen electrode is observed compared with that 
of the initial structure shown in Fig. 1e. Hence, the study shows 
that it seems feasible to achieve stable long-term operation of 
SOEC prepared without cobalt at high efficiency (thermoneutral 
conditions) with a H2 production rate of 3.48 ml min⁻¹ cm⁻² at a 
temperature enabling use cheap steels. 57 This is important for 
reducing overall cost of the unit and for competing favorably 
with alkaline electrolysis cells, which may be operated at the 
same area-specific production capacity but typically at a 
somewhat lower electrical efficiency.58

4. Conclusions

In summary, the activity of an LSF-based oxygen electrode for 
both the ORR and the OER has been strongly enhanced by 
applying a nanoporous hybrid catalyst coating composed of 
nanoparticles of CGO and Pr$_6$O$_{11}$. The coating was realized using 
infiltarion with a solution of colloidal CGO nanocrystals and 
Pr(NO$_3$)$_3$. The hybrid-catalyst-coated LSF oxygen electrode 
exhibited a polarization resistance as low as 0.017 $\Omega \cdot cm^2$ at 750 
°C, about one order of magnitude lower than that of bare LSF 
(0.197 $\Omega \cdot cm^2$). Furthermore, the activity of the hybrid-catalyst-
coated LSF electrode for both the ORR and the OER was 
investigated in fuel-electrode-supported cells under practical 
operating conditions. Excellent performance and durability 
were observed. The analyses of SEM, BET, ECR as well as EIS 
indicated that the Pr$_6$O$_{11}$ greatly accelerates the oxygen surface 
exchange kinetics and the nanoporous architecture of the 
catalyst coating significantly increases the surface area for the 
oxgen incorporation reaction, thus enabling the superior 
activity and durability. This work shows that well performing 
cobalt-free oxygen electrode can be prepared and that when 
applied on a CGO20-coated Ni/YSZ electrode supported cell 
stable operation at 650 °C under -0.5 A cm⁻² with cell voltage 
close to 1.3 V can be achieved.
Conflicts of interest
There are no conflicts to declare.

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