



Performance and stability of $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ cathode promoted with palladium based catalysts in solid oxide fuel cells

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ABSTRACT

The effect of catalyst loading, operation temperature and co-infiltration of the palladium-based catalysts on the performance and stability of $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSM) cathode of solid oxide fuel cells (SOFCs) is investigated. The result shows that adding a small amount of Pd catalyst (0.08 mg cm^{-2}) has a remarkable effect on the reduction of overpotential of LSM cathodes and high palladium loading is detrimental to the electrochemical activity of LSM cathodes. The performance and stability of the Pd-impregnated LSM cathodes can be enhanced significantly by co-infiltration of palladium with either 20 mol% of silver or 5 mol% of cobalt. Increased stability of the co-infiltrated catalyst materials is probably related to the enhanced resistance of the co-impregnated $\text{Pd}_{0.95}\text{Co}_{0.05}$ and $\text{Pd}_{0.8}\text{Ag}_{0.2}$ nanoparticles against agglomeration and sintering at SOFC operation temperatures. The results indicate the co-impregnation is effective not only to enhance the electrochemical activity but also to improve the stability of LSM cathodes for the O_2 reduction reaction of SOFCs.

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1. Introduction

Lanthanum strontium manganite (LSM) is one of the most widely studied cathode materials for solid oxide fuel cells (SOFCs) due to its high electronic conductivity, high electrocatalytic activity for the O_2 reduction at high temperature and proven structural stability and thermal compatibility with $\text{Y}_2\text{O}_3\text{-ZrO}_2$ (YSZ) electrolyte [1]. However, when the operation temperature of the SOFCs is lowered to the intermediate temperature range of 600–800 °C in order to increase the performance long-term stability and widen the materials selectivity, the area specific resistance (ASR) and overpotential of LSM electrodes for the O_2 reduction reaction increase sharply due to the fact that LSM is almost a pure electronic conductor with negligible oxygen ion conductivity [2], and the three phase boundary (TPB) for the reaction is limited to the electrode/electrolyte interface [3–5]. Mixing LSM with ionic conducting phase of YSZ or Gd-doped ceria (GDC) can extend the TPB into the electrode bulk and reduce the ASR of the cathodes for the O_2 reduction reaction [6–9].

Application of metal catalysts into the microstructure of SOFC electrodes has shown a considerable effect in lowering the overpo-

tential and increasing the performance of the fuel cells [10–13]. Recently, Vohs and Gorte gave a comprehensive review on the infiltrated SOFC cathodes [14]. Among different metallic catalyst materials that have been investigated for using in SOFC cathodes, Pd has shown significant effect on the promotion of the electrochemical activity for the O_2 reduction especially at lower temperatures [15,16]. Erning et al. [17] reported a considerable increase in the current density by addition of Pd catalyst into LSM cathodes, much better than the improvement by Pt. In contrast, Haanappel et al. [18] reported no improvement after introduction of Pd to the LSM electrode. Liang et al. [19] studied the phase transformation of Pd and found that PdO transforms to metallic Pd at temperatures above 830 °C in air and the promoting effect of impregnated Pd on the oxygen reduction reaction was observed at temperatures below and above this phase transition temperature. This indicates that both palladium and palladium oxide are beneficial for the catalytic promotion of the O_2 reduction reaction at the cathodes of SOFCs. Our recent work on the catalytic effects of Pd on the hydrogen oxidation reaction on Ni/GDC and $(\text{La,Ca})(\text{Cr,Mn})\text{O}_3$ (LCCM)/GDC anodes shows that the presence of Pd/PdO nanoparticles may be the main reason for the enhancement of the adsorption and diffusion of the hydrogen species on the electrode surface for the reaction [20,21]. However, the stability of the impregnated metal nanoparticles is a serious concern due to the inevitable agglomeration and grain growth of the nanoparticles under the high operation temperature of SOFCs. The grain growth and agglomeration of the impregnated

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metal catalyst nanoparticles are believed to be the main reason for the observed degradation in the performance stability of the electrodes containing metal catalyst [10,19,22,23].

Thus, it is important to investigate the performance and stability of the Pd-based catalysts-impregnated LSM cathode and to develop more stable Pd-based catalysts. Co-impregnation or co-infiltration of two or more catalytic species could effectively inhibit the grain growth and agglomeration of catalytic nanoparticles. In this report, the performance and stability of LSM cathodes impregnated with Pd, Pd_{1-x}M_x (M=Co, Mn and Ag; x=0.05 and 0.20) were studied at temperatures range of 700–850 °C. The effect of catalyst loading was also examined. The results indicate that co-infiltrated Pd-based catalysts enhance the performance and stability of the LSM cathodes for the oxygen reduction reactions of SOFCs.

2. Experimental procedure

Dense electrolyte substrates were prepared from 8 mol% yttria stabilized zirconia (YSZ, Tosoh Co., Japan) by die pressing, followed by sintering at 1500 °C for 4 h. Thickness and diameter of the final YSZ pellets were 0.7 and 19 mm respectively. In order to enhance the adhesion between the electrode and the YSZ electrolyte, both sides of the pellets were ground with sandpaper. La_{0.8}Sr_{0.2}MnO₃ (LSM, Fuel Cell Materials Inc., USA) powder was mixed with Ink Vehicle 500 (Fuel Cell Materials Inc., USA) and 5 wt% graphite to increase the porosity of the cathode. The slurry was applied on to the YSZ electrolyte by slurry painting method. The surface area of the electrode was 0.5 cm². LSM electrode was sintered at 1100 °C for 2 h and the final thickness of the electrode coating was ~35 μm.

Platinum paste (Metalor Co., Swiss) was painted on the other side of YSZ pellets as the counter and reference electrodes. Counter electrode was painted opposite to the LSM electrode with the same surface area as the LSM electrode and the reference electrode was painted as a circle with a 4 mm gap between the counter and reference electrodes. Painted platinum was baked at 850 °C for 15 min in air. Platinum mesh in direct contact with the LSM electrode was used as the current collector.

Pd(NO₃)₂ and Pd_{1-x}M_x(NO₃)₂ (M=Co, Mn and Ag; x=0.05 and 0.2) impregnation solution were prepared from Pd(NO₃)₂·xH₂O, Co(NO₃)₂·6H₂O, AgNO₃·xH₂O and Mn(NO₃)₂·xH₂O nitrate solutions (all from Sigma–Aldrich). The concentration of the impregnation solution was 1 M. In the impregnation method a droplet of the catalyst solution was placed on the top surface of porous electrode and the capillary force caused the infiltration of the solution into the open pores of the electrode. The excess solution was wiped out using a soft tissue. The cells were heated at 700 °C for the deposition of the impregnated catalyst solution and for the formation of the Pd or PdO-based nanoparticles in the LSM electrode structure. Loading of catalytic agent was measured by weighting the specimen before and after the impregnation treatment and expressed as weight percentage of PdO. With the concentration of the solution used, each impregnation treatment yielded ~0.08 mg cm⁻² loading of the PdO catalysts. The high catalyst loading was achieved by repeating the impregnation treatment. In the present study, cathode samples with 0.08 and 0.25 mg cm⁻² catalyst loading were used to investigate the effect of catalyst loading on the performance and stability of the cathodes. The phase of impregnated palladium nanoparticles calcined at temperature ranges of 800–900 °C was determined by X-ray diffraction (XRD, Shimadzu, XRD-6000, X-Ray Diffractometer) using CuK_{α1} radiation (λ = 1.54060 Å) at room temperature. X-ray scans were run over a 2θ spectrum of 20–80° at a scan rate of 4°/min.

Electrochemical measurements were carried out using an Autolab PGSTAT302 potentiostat. A three electrode system comprising working, counter and reference electrodes was used for the electrochemical measurements. Cell arrangement is similar that explained in [24,25]. The electrochemical impedance spectra were measured at open circuit potential in the frequency range of 0.1 Hz–100 kHz with signal amplitude of 10 mV. Polarization was performed under current density of 100 and 200 mA cm⁻² at testing temperatures of 750 °C and 850 °C, respectively. All three electrodes were exposed to open air. The performance stability of the impregnated LSM cathodes was carried out at 750 °C and 850 °C for 44 h. Ohmic resistance of the cell was measured from the high frequency intercept of the impedance curves in Nyquist plots and electrode polarization resistance or area specific resistance (ASR) was obtained from the differences of the high and low frequency intercepts. Microstructure of the LSM cathode was examined using a JEOL 6340F field emission scanning electron microscope.

3. Results and discussion

3.1. Effect of PdO catalyst loading

It is well known that the effectiveness of palladium as oxidation catalysts depends strongly on its complex reaction with gas-phase oxygen to form surface PdO or nonstoichiometry PdO_x and on the

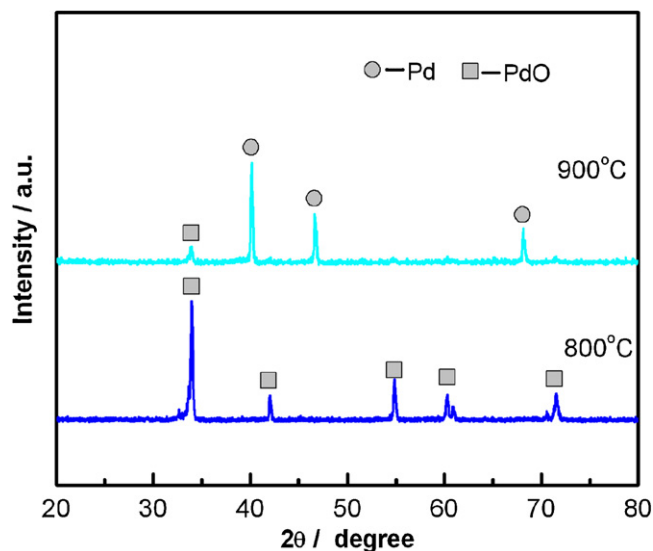


Fig. 1. XRD spectra for palladium oxide samples heat treated at 800 and 900 °C in air for 1 h.

redox reactions, which in turn is a complex function of temperature and oxygen partial pressure [26,27]. Our early TGA results indicate that there is a phase transfer between PdO and metallic Pd at a temperature of about 830 °C in air [19]. Thus it is interesting and important to study the chemical states of the palladium catalyst at the test conditions of this study. Fig. 1 shows the XRD spectra for the palladium samples heat-treated at 800 and 900 °C in air. The results show that at 800 °C palladium primarily exists in the form of PdO. This is consistent with the observations that the impregnated palladium mainly exists as PdO in the case of Pd-impregnated LSM/YSZ composite cathode calcined at 750 °C [28]. As the temperature increased to 900 °C, metallic palladium species is dominant, however a trace of PdO is also observed. This indicates that the impregnated palladium nanoparticles in the LSM cathode may exist as Pd/PdO or nonstoichiometry PdO_x, depending on the temperature (750–850 °C in the present study) and oxygen partial pressure, which in turn is related to the overpotential or current in the case of fuel cell reactions. Thus, it should be emphasized here that the use of Pd catalysts and PdO catalysts loading instead of Pd/PdO or PdO_x catalysts in the present study is for the purpose of simplicity.

The effect of PdO catalyst loading on the performance and stability of the LSM cathode was studied on the electrodes impregnated with 0.08 mg cm⁻² and 0.25 mg cm⁻² PdO catalysts. Fig. 2 is the impedance spectra for the O₂ reduction reaction on Pd-impregnated LSM electrodes before and after the polarization treatment at 850 °C and 200 mA cm⁻² in air for 2, 22 and 44 h. For the pure LSM electrode without palladium impregnation the electrochemical impedance responses are characterized by a large and depressed impedance arc and the area specific resistance (ASR) of the LSM electrode is 2.05 Ω cm² before the polarization treatment (Fig. 2a). With the polarization treatment at 200 mA cm⁻², the impedance arc decreased significantly and after polarized for 44 h, the ASR decreased to 0.15 Ω cm², much smaller than 2.05 Ω cm² at the beginning of the polarization treatment. The significant reduction in the ASR for the reaction on the LSM cathode with the polarization treatment is clearly due to the activation effect of the polarization on the electrocatalytic activity of LSM-based cathode [25,29]. The impedance responses after polarized for 44 h (inset graph, Fig. 2a) clearly show the separation and existence of three semicircles at high, medium and low frequencies, indicating the presence of at least three electrode steps for the O₂ reduction on

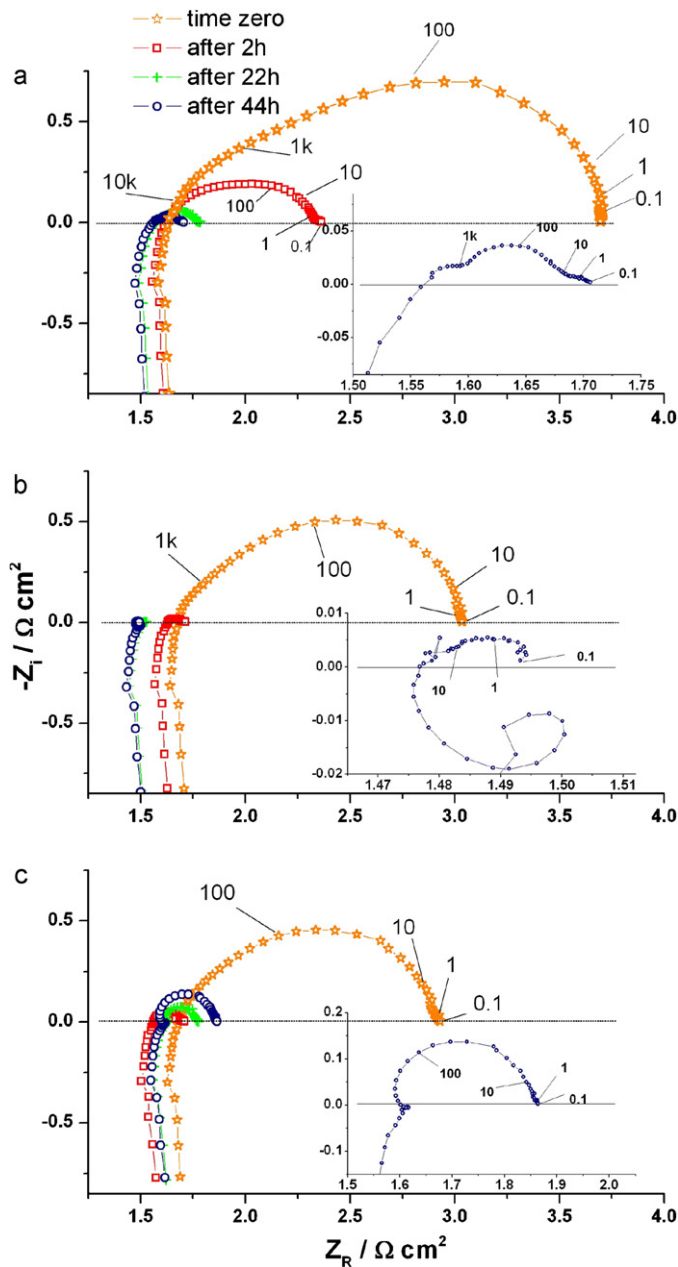


Fig. 2. Electrochemical impedance spectra for the O_2 reduction reaction on (a) pure LSM electrode, (b) 0.08 mg cm^{-2} Pd-impregnated LSM and (c) 0.25 mg cm^{-2} Pd-impregnated LSM at 850°C . The impedance curves were measured at open circuit before and after polarized at 200 mA cm^{-2} for different period. The inset shows enlarged graph of the impedance spectrum after polarized for 44 h. The numbers in the figure are frequencies in hertz.

LSM cathode at 850°C , consistent with previous results [30,31]. The existence of three semicircles in the impedance spectra for the reaction on the LSM-based cathodes is also reported by others [32]. For the LSM electrode impregnated with 0.08 mg cm^{-2} PdO catalyst loading, the impedance arc also decreased significantly and after polarization at 200 mA cm^{-2} for 44 h the ASR is $0.018 \Omega \text{ cm}^2$ (inset graph, Fig. 2b), 8 times smaller than $0.15 \Omega \text{ cm}^2$ measured on pure LSM under identical polarization treatment conditions. For the LSM electrode with a higher PdO loading of 0.25 mg cm^{-2} , the ASR after polarization at 200 mA cm^{-2} for 44 h is $0.28 \Omega \text{ cm}^2$ (inset graph, Fig. 2c), even higher than $0.15 \Omega \text{ cm}^2$ measured on pure LSM under identical polarization treatment conditions. This shows that high palladium catalyst loading is detrimental to the electrochemical activity of SM cathode and this may be the reason for the contradic-

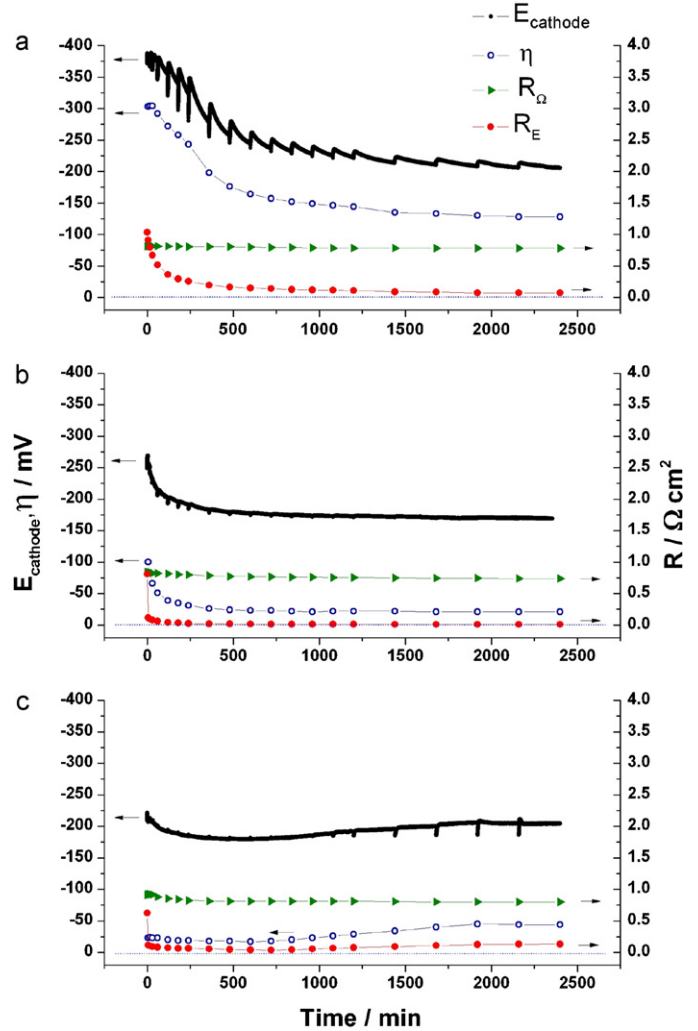


Fig. 3. Polarization performance for (a) pure LSM electrode, (b) 0.08 mg cm^{-2} Pd-impregnated LSM and (c) 0.25 mg cm^{-2} Pd-impregnated LSM at 850°C and 200 mA cm^{-2} for 44 h in air.

tory reports regarding the enhancement of palladium to the activity of LSM cathodes [17,18].

Fig. 3 shows the polarization curves for LSM cathodes at low and high loading of Pd catalyst at 850°C and 200 mA cm^{-2} . The electrode polarization resistance, R_E and ohmic resistance, R_Ω were obtained from the electrochemical impedance curves and overpotential, η , was obtained by subtracting the iR losses from the measured cathodic polarization potential, E_{cathode} . Similar to the impedance behavior, polarization potential for the O_2 reduction on pure and Pd-impregnated LSM cathodes decreased significantly with the cathodic polarization (Fig. 3a). For the reaction on a 0.08 mg cm^{-2} Pd-impregnated LSM, the cathode overpotential is 21 mV after polarized for 44 h (Fig. 3b), significantly smaller than 130 mV in the case of pure LSM cathode measured under the same polarization conditions. This indicates that the addition of the Pd/PdO nanoparticles significantly promotes the electrocatalytic activity of the LSM cathode. In the case of LSM with high catalyst loading of 0.25 mg cm^{-2} the initial overpotential is low, 17 mV under a cathodic current of 200 mA cm^{-2} , but it gradually increases with the polarization and finally reached $\sim 44 \text{ mV}$, which is higher than 21 mV for the reaction on a LSM with a low PdO catalyst loading of 0.08 mg cm^{-2} . This shows that high catalytic loading is not beneficial for the stability of the electrocatalytic activity of the LSM cathode.

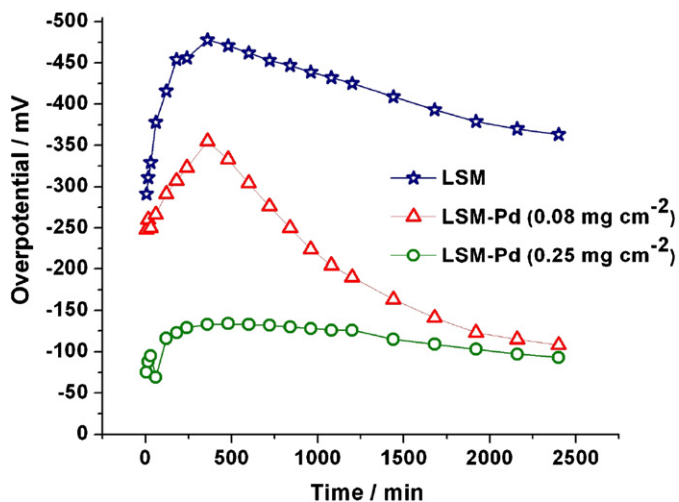


Fig. 4. Plots of cathode overpotential versus time for pure LSM, 0.08 mg cm⁻² Pd-impregnated LSM and 0.25 mg cm⁻² Pd-impregnated LSM at 750 °C and 100 mA cm⁻².

The polarization behavior of LSM cathode without and with Pd impregnation was also studied at 750 °C and 100 mA cm⁻². Fig. 4 shows the plots of overpotential of the O₂ reduction reaction on pure LSM and Pd promoted LSM electrodes with different PdO catalyst loadings at 750 °C. The cathode overpotential increased with the polarization time and reached a maximum after polarized for ~500 min, followed by a steady decrease with the polarization time. The dependence of the overpotential on the polarization time appears to be different from that observed at a higher temperature of 850 °C. At this stage the reason for the appearance of the maximum peak of the overpotential with the current passage time is not clear. Similar to that observed at 850 °C addition of Pd catalysts also remarkably decreases the overpotential of the reaction on LSM cathode at 750 °C. In the case of pure LSM, the overpotential for the reaction after polarization for 44 h is ~400 mV, significantly higher than ~100 mV for 0.08 mg cm⁻² Pd-impregnated LSM and ~90 mV for 0.25 mg cm⁻² Pd-impregnated LSM. Pure Co, Mn and Rh were also infiltrated to the LSM cathode, but no remarkable enhancing effect was observed.

3.2. Effect of co-infiltration with Co, Mn and Ag

Cobalt, manganese and silver were co-infiltrated with palladium during the impregnation treatments. Fig. 5 shows plots of overpotential versus polarization time for the LSM cathodes impregnated with Pd–Mn, Pd–Co and Pd–Ag solutions with composition of 5 and 20 mol% of co-infiltrated Mn, Co and Ag, measured at 850 °C and 200 mA cm⁻². The infiltrated catalyst loading is 0.08 mg cm⁻². The overpotential data for Co and Mn impregnated LSM cathode is also included in Fig. 5 for comparison. As shown in Fig. 5, the performance and stability of the catalyst impregnated LSM cathodes depend strongly on the composition of the Pd–Mn, Pd–Co and Pd–Ag catalyst solutions. In the case of Pd–Mn and Pd–Co, Pd_{0.95}Mn_{0.05} and Pd_{0.95}Co_{0.05}-infiltrated LSM cathodes show a substantially low overpotential for the O₂ reduction reaction as compared to that on pure Co and Mn and on the Pd_{0.8}Mn_{0.2} and Pd_{0.8}Co_{0.2}-infiltrated LSM cathodes. The reason may be due to the low solubility of cobalt and manganese oxides with palladium and in the case of the Pd_{0.8}Mn_{0.2} and Pd_{0.8}Co_{0.2}-infiltrated LSM, cobalt and manganese oxides could be segregated and co-exist with palladium [33]. The segregated cobalt and manganese oxides are not electrocatalytically active for the O₂ reduction reaction at high temperatures, resulting in the high overpotential,

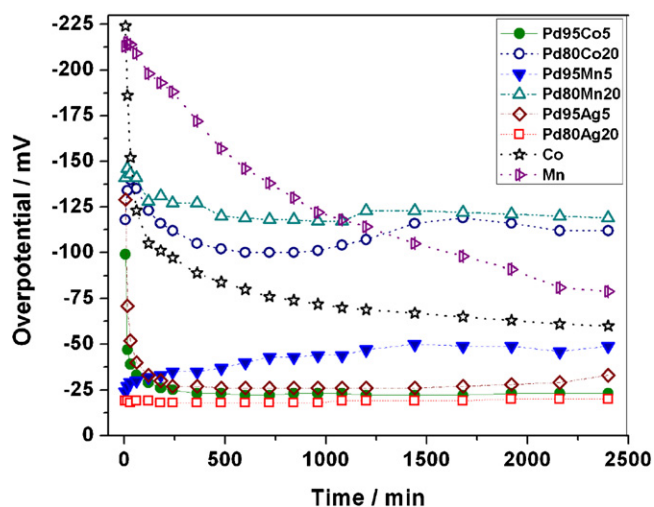


Fig. 5. Plots of cathode overpotential as a function of polarization time for the LSM cathode co-impregnated with Pd–Mn, Pd–Co and Pd–Ag with 5 and 20% Mn, Co and Ag in the impregnation solution. The catalyst loading was 0.08 mg cm⁻² and polarization was carried out at 850 °C and 200 mA cm⁻².

as shown by the high overpotentials of Co and Mn-impregnated LSM cathodes (Fig. 5). Sholkplapper et al recently [34] investigated the performance of Ag–LSM cathode electrode and showed the enhancement of infiltrated Ag to the activity of LSM cathodes. Both Pd_{0.95}Ag_{0.05} and Pd_{0.8}Ag_{0.2} infiltrated LSM cathodes show good performance and stability, indicating the co-impregnation of Pd and Ag may result in alloy formation, leading to the improved long term stability of the Pd-based catalyst [35]. The best performance and performance stability were observed on the LSM cathodes impregnated with 0.08 mg cm⁻² Pd_{0.95}Co_{0.05} and Pd_{0.8}Ag_{0.2}. The degradation in performance for the O₂ reduction reaction is negligible.

Fig. 6 is the plots of the overpotential for the O₂ reduction reaction on LSM cathodes impregnated with Pd, Pd_{0.95}Co_{0.05} and Pd_{0.8}Ag_{0.2} catalyst as a function of polarization at 200 mA cm⁻² and 850 °C (Fig. 6a) and 100 mA cm⁻² and 750 °C (Fig. 6b). The catalyst loading was 0.25 mg cm⁻². At 850 °C, performance of the Pd-impregnated LSM cathode showed the stable performance for the initial ~700 min and then degraded significantly with the polarization time (Fig. 6a), indicating the instability of Pd-impregnated LSM cathode. The significant increase in the overpotential for the reaction on Pd-impregnated LSM cathodes is most likely due to the significant grain growth of impregnated Pd/PdO nanoparticles. The performance stability of the both Pd_{0.95}Co_{0.05} and Pd_{0.8}Ag_{0.2}-infiltrated LSM cathodes improved significantly and there is basically no significant change in the overpotential during the polarization period of 2500 min at 850 °C. In the case of Pd_{0.95}Co_{0.05}-infiltrated LSM cathode, cobalt could substitute palladium site to form Pd_{0.95}Co_{0.05}O solid solutions, similar to Pd_{0.95}Mn_{0.05}O as reported early [19]. For Pd–Ag system, the formation of PdAg solid solution occurs in a wide range of Pd and Ag compositions [36]. Thus the good stability of the Pd_{0.95}Co_{0.05} and Pd_{0.8}Ag_{0.2}-infiltrated LSM cathodes could be attributed to the formation of Pd_{0.95}Co_{0.05}O and Pd_{0.8}Ag_{0.2}O solid solution nanoparticles. Similar results were also observed for the reaction at 750 °C (Fig. 6b). The co-infiltration of Pd_{0.8}Ag_{0.2} and Pd_{0.95}Co_{0.05} catalysts not only increases the electrocatalytic activity of the LSM cathode for the O₂ reduction reaction but also enhances significantly the performance stability. As shown in Fig. 6, LSM cathodes impregnated with Pd_{0.8}Ag_{0.2} and Pd_{0.95}Co_{0.05} catalysts show significantly lower overpotential and are stable over the test period of 44 h at both 750 and 850 °C. LSM cathode impregnated with Pd_{0.8}Ag_{0.2} cat-

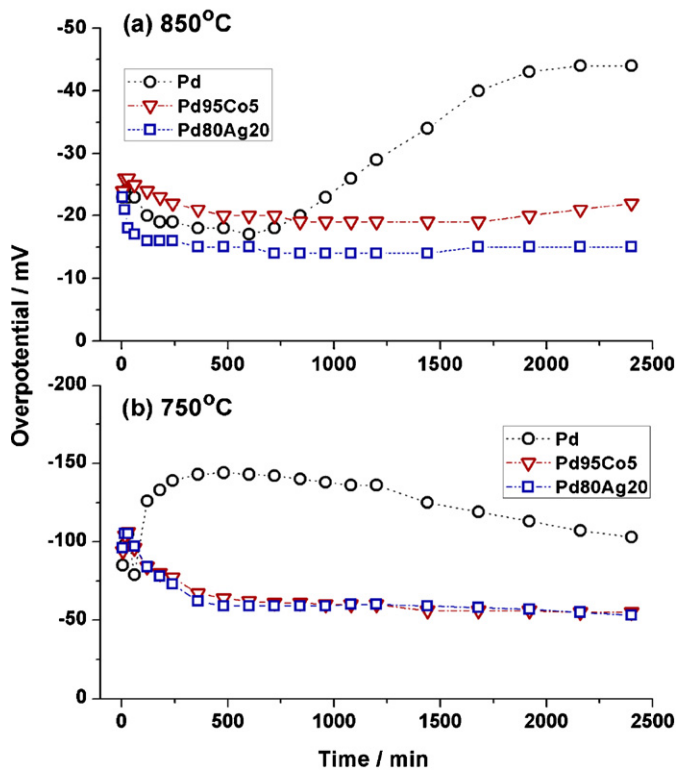


Fig. 6. Plots of cathode overpotential as a function of polarization time for LSM cathode impregnated with Pd, Pd_{0.95}Co_{0.05} and Pd_{0.8}Ag_{0.2} catalyst at (a) 850 °C and 200 mA cm⁻² and (b) 750 °C and 100 mA cm⁻². The catalyst loading was 0.25 mg cm⁻².

alysts showed a slightly better performance as compared to that impregnated with Pd_{0.95}Co_{0.05} catalysts especially at 850 °C.

3.3. Microstructure of the impregnated LSM electrodes

The microstructure of Pd and co-infiltrated LSM electrodes was examined by SEM. Fig. 7a shows SEM micrograph of palladium particle distribution on the surface of a 0.08 mg cm⁻² Pd-impregnated LSM cathode before the polarization test. PdO particles with particle size of ~20 nm on the surface of LSM grains were observable. After polarization test at 100 mA cm⁻² and 750 °C for 44 h, PdO particles grow and the average particle size is around 30–40 nm (Fig. 7b). With the increase of the operation temperature to 850 °C the Pd catalyst particles grow significantly to 70–90 nm after polarized for 44 h for the reaction on the Pd-impregnated LSM with the same PdO loading of 0.08 mg cm⁻² (Fig. 7c). In the case of Pd-impregnated LSM electrodes with a high PdO loading of 0.25 mg cm⁻², significant agglomeration of the catalyst particles can be seen after polarized at 850 °C for 44 h (Fig. 7d). The size of the agglomerates is as high as 1200 nm. For the Pd promoted LSM electrode system, the growth and agglomeration of Pd catalyst particles at 850 °C is significant as compared to that operated at 750 °C. This shows that the grain growth and agglomeration depend strongly on the operation temperature as well as the catalyst loading. Agglomeration and sintering of the catalyst particles decreases the active surface area of the catalyst and consequently decreases catalytic activity for the oxygen reduction process. This explains the significant overpotential increase for the O₂ reduction reaction on the 0.25 mg cm⁻² Pd-impregnated LSM cathodes polarized at 200 mA cm⁻² and 850 °C (Fig. 6a).

Grain growth was also observed for the co-infiltrated LSM electrodes. Fig. 8a shows SEM micrograph of a 0.25 mg cm⁻²

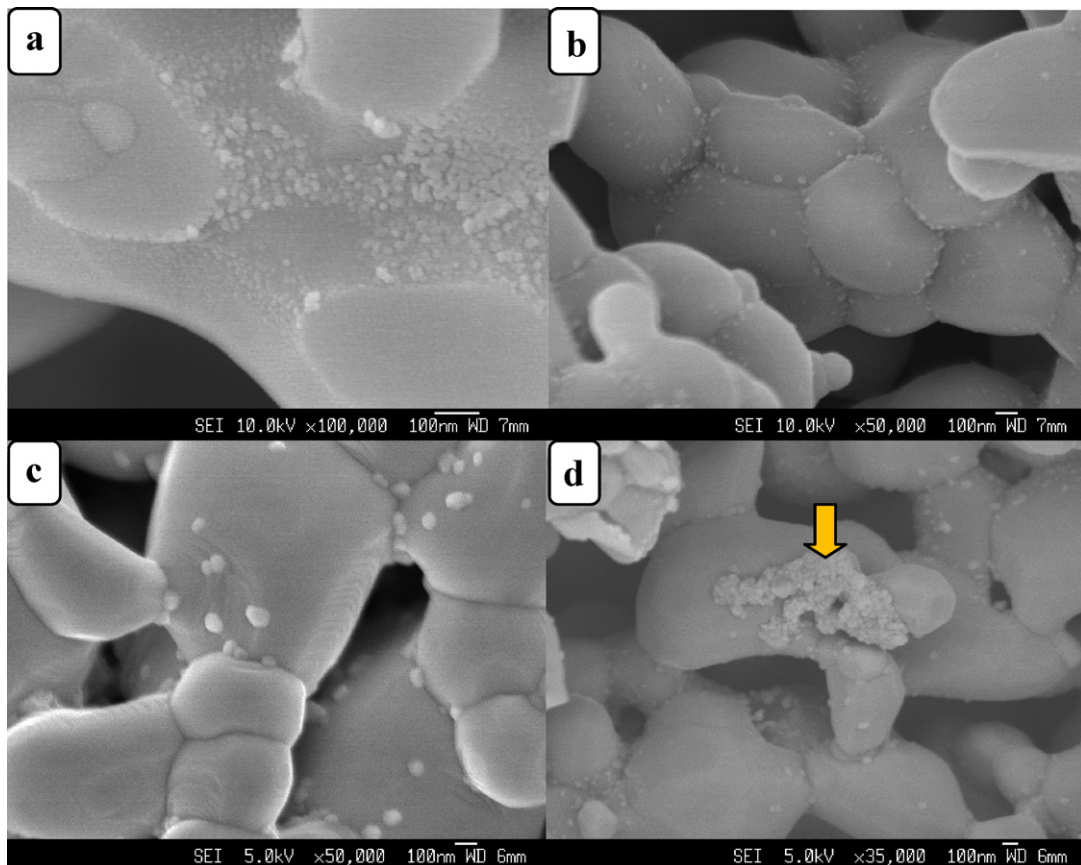


Fig. 7. SEM micrograph of Pd-impregnated LSM cathode with (a) 0.08 mg cm⁻² PdO before polarization, (b) 0.08 mg cm⁻² PdO after polarization at 750 °C for 44 h, (c) 0.08 mg cm⁻² PdO after polarization at 850 °C for 44 h and (d) 0.25 mg cm⁻² PdO after polarization at 850 °C for 44 h.

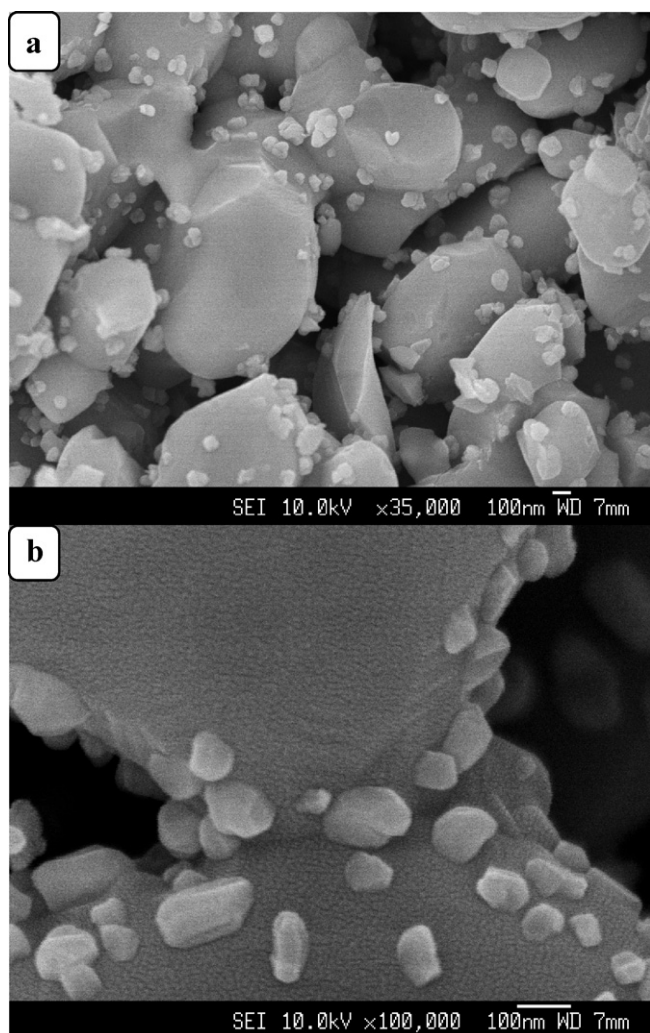


Fig. 8. SEM micrograph of 0.25 mg cm^{-2} $\text{Pd}_{0.8}\text{Ag}_{0.2}$ -impregnated LSM cathode after polarization at 850°C and 200 mA cm^{-2} for 44 h. The high magnification picture is shown in (b).

$\text{Pd}_{0.8}\text{Ag}_{0.2}$ -infiltrated LSM electrode after polarized at 200 mA cm^{-2} and 850°C for 44 h. The size of the $\text{Pd}_{0.8}\text{Ag}_{0.2}\text{O}$ catalyst particles grew to 70–100 nm, significantly larger than the original size of $\sim 20 \text{ nm}$ (the original particle size of $\text{Pd}_{0.8}\text{Ag}_{0.2}\text{O}$ was similar to PdO, see Fig. 7a). However, different from 0.25 mg cm^{-2} Pd-infiltrated LSM cathode (see Fig. 7d), there is no significant agglomeration of infiltrated $\text{Pd}_{0.8}\text{Ag}_{0.2}\text{O}$ catalytic particles. $\text{Pd}_{0.8}\text{Ag}_{0.2}\text{O}$ particles are uniformly distributed on the LSM grain surface and LSM grain boundaries (Fig. 8a). Presence of well separated individual $\text{Pd}_{0.8}\text{Ag}_{0.2}\text{O}$ particles in the LSM cathodes is likely the reason for the enhanced stability of the LSM cathode with co-infiltrated catalyst. On the other hand, there is a formation of distinct crystal facets on the $\text{Pd}_{0.8}\text{Ag}_{0.2}\text{O}$ catalyst nanoparticles (see Fig. 8b). The presence of crystal facets on the catalyst nanoparticles could be beneficial for the O_2 reduction reaction, similar to the high activity reported for the O_2 reduction reaction on faceted Pt nanoparticles in proton exchange membrane fuel cells [37].

Bidrawn et al. [38] reported that the calcination temperature of the LSM/YSZ cathode influences the catalytic effect of added dopants on the LSM/YSZ cathodes and concluded that the observed enhancing effect as a result of addition of a catalyst agent is associated with electrode structure, and not the electrochemical or catalytic activity enhancement. Other reports correlate the performance enhancements to the catalytic activity of the infiltrated

materials [10,39]. The fact that sputtering of a very thin layer of Pt metal on the surface of cathode electrode cause a significant enhancement in cathode overpotential [39] suggest that change in electrode structure might not be the only reason for performance enhancement. The likely existence of Pd/PdO or nonstoichiometry PdO_x on the surface of impregnated palladium nanoparticles (see Fig. 1) implies that spillover of the gas molecules over the palladium catalytic nanoparticles is probably one of the major enhancement mechanisms in palladium-based catalyst promoted electrodes as reported early [20,21].

4. Conclusions

Performance and stability of LSM cathode electrode impregnated with Pd, Pd–Mn, Pd–Co and Pd–Ag were investigated at catalyst loadings of 0.08 and 0.25 mg cm^{-2} and operation temperatures of 750 and 850°C . Addition of 0.08 mg cm^{-2} PdO to LSM cathode substantially decreases the cathode overpotential from 130 mV to 21 mV and the performance of the cell is quite reasonable during 44 polarization of the cell. High catalyst loading of 0.25 mg cm^{-2} is detrimental to the performance stability in particular at operation temperature of 850°C . The instability is mainly due to the significant agglomeration and grain growth of palladium catalyst nanoparticles at SOFC operation temperature. Co-impregnation of Pd with Mn, Co and Ag mitigates the agglomeration and sintering, and among the catalyst systems tested, $\text{Pd}_{0.8}\text{Ag}_{0.2}$ and $\text{Pd}_{0.95}\text{Co}_{0.05}$ compositions show significantly enhanced performance and good stability. In the case of LSM impregnated with $\text{Pd}_{0.8}\text{Ag}_{0.2}$ nanoparticles, the formation of special crystallographic orientation and facets on the surface of $\text{Pd}_{0.8}\text{Ag}_{0.2}$ nanoparticles could also be beneficial for the O_2 reduction reaction. The results indicate the co-impregnation is effective to enhance the activity and stability of SOFC cathodes.

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