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Can Silver Be a Reliable Current Collector for Electrochemical Tests?

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The true functionality of a current collector employed in electrochemical cells is to ensure a low-resistance steady electrons flow between the cell and instrumentation without involving in any local electrochemical reactions of the electrode. In this study, we investigated the effect of curing temperature of a common current collector, silver, on the polarization area specific resistance (ASR) of a cathode. The results explicitly showed that at least one order of magnitude lower ASR for a cathode with Ag cured at 800°C than that cured at 650°C of the same cathode configuration. Microscopic analysis of the 800°C-cured cells revealed a deep penetration and abundant distribution of Ag into the cathode/electrolyte interfacial region. These finely dispersed and highly conductive Ag particles/agglomerates are ORR (oxygen reduction reaction)-active, thus engaging in the local electrochemical reaction and overshadowing the true properties of the cathode under investigation. Based on these results, we call for caution when using Ag as a current collector for electrochemical measurements, particularly at a temperature $\geq 650^\circ\text{C}$.

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Recent efforts in the development of solid oxide fuel cells have been focusing on exploring new electrode materials and optimizing microstructure.¹⁻⁴ A general strategy to evaluate the performance of an electrode in a laboratory setting is to study its electrochemical behaviors in symmetrical cell or single cell configuration with either DC conductivity or AC impedance technique. In order to fulfill the electrical connection between the electrode and external instrumentation, a pair of metallic films necessary for collecting current is typically applied to the surfaces of the electrode. A good current collector should act solely as an interfacial electronic conductor to relay electrons from the cell to the measuring instrument; it should not participate in any local electrochemical reactions of the electrodes.^{5,6} So far, the most popular current collectors of choice in electrochemical characterizations are found among noble metals such as Ag, Pt, and Au. In particular, Ag is a favored choice for cathode studies below 800°C because of its affordable cost and high electronic conductivity.⁷⁻¹⁵

On the other hand, silver is also known for its excellent oxygen reduction reaction (ORR) activity. Therefore, it has been intentionally utilized as a performance enhancer for cathodes La(Sr)Fe(Co)O₃ (LSCF), La(Sr)FeO₃ (LSF) and La(Sr)CoO₃ (LSCo) in SOFC research.^{8,16-19} However, due to its low melting temperature (962°C) and high vapor pressure,¹⁰ silver has a great propensity to be volatile and mobile at elevated temperatures.²⁰ If Ag migrates into the cathode microstructure as a result of its high mobility, and gets involved in the local electrochemical reactions, its known excellent ORR catalytic activity could overshadow the true performance of the cathode under investigation, resulting in misleading conclusions. Therefore, use of Ag as a cathode current collector at elevated temperatures should proceed with caution. Despite early reports on the variability of cathode performance with noble-metal current collectors in long-term testing,¹⁰ this view has not been properly recognized in the solid state electrochemistry community.

In this study, we demonstrate the effect of curing temperature of silver current collector on the electrochemical performance of LSCF-based cathodes in short-term testing like temperature-dependence evaluation of ASR. We also show that Pt can be a more reliable current collector than Ag for cathode performance evaluations.

Experimental

Fabrication of symmetrical cells.— A symmetric cell configuration of LSCF+GDC/LSGM/LSCF+GDC, in which LSGM and GDC denote La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.17}O_{3-δ} and Ce_{0.8}Gd_{0.2}O₂, respectively, was employed for this study. The LSGM electrolyte was fabricated by standard tape casting method. In brief, LSGM powder was synthesized by

conventional solid state reaction as described elsewhere.²¹ The slurry formulation was prepared by intimately mixing the LSGM powder with a desired amount of solvent (Terpineol, Aldrich), dispersant (Hypermer, Croda), binder (Ethyl cellulose, Acros) and plasticizer (Diocetyl phthalate, Acros). The slurry was degassed under vacuum and then casted on the silicone-coated Mylar layer using a commercial tape caster. After drying in air, the green tape was cut into $\phi 20$ mm circles, thermally laminated and sintered at 1450°C for 6 h. The final LSGM electrolyte was 15 mm in diameter and approximately 150–200 μm in thickness.

A commercial LSCF+GDC paste purchased from Fuel Cell Material (LSCFGDC-1, sku: 232202) was screen printed on both sides of the electrolyte to serve as the cathode. The resulting tri-layer was then fired at 1100°C for 1 hour to complete the fabrication of a symmetrical cell. The effective area and thickness of a cathode are 0.75 cm² and ~ 30 μm , respectively.

Current collector preparation.— Two types of current collectors were employed in this study: Ag paste (C8829, Heraeus) with Ag mesh and Pt paste (CL11-5100, Heraeus) with Pt mesh. To prepare the current collector, a thin layer of paste was first screen printed on the cathode area, and the metal mesh was then gently pressed into contact with the paste layer. Two curing temperatures were studied for the Ag current collectors: 800 and 650°C with curing duration of 1 hour at each temperature. Pt current-collector was pre-fired at 950°C for 30 min before test.

Characterization.— Electrochemical Impedance spectroscopy (EIS) was utilized as a tool to study the performance of cathode in a symmetrical cell configuration mentioned above. EIS measurements were carried out on the symmetrical cells using an electrochemical workstation (IM6, Zahner) under open circuit conditions from 550 to 800°C in a step of 50°C. The frequency was swept from 10⁵ to 0.05 Hz with AC stimulus voltage amplitude of 10 mV. To avoid variability, two identical cells with different types of current collectors were loaded side-by-side in the same furnace and measured in sequence. The measured EIS spectra were deconvoluted with the Thale equivalent circuit software (Zahner). The obtained polarization resistance was then divided by two and normalized to the cathode area to acquire the actual cathode polarization ASR. Microstructures of the tested cells were examined by a field emission scanning electron microscope (FESEM, Zeiss Ultra) equipped with an energy dispersive X-ray spectroscopy (EDS) analyzer.

Result and Discussion

The effect of Ag curing temperature.— The effect of Ag curing temperature on the polarization ASR of the cathode is shown in Fig. 1 for 550, 600 and 650°C. First, the cell with Ag cured at 800°C

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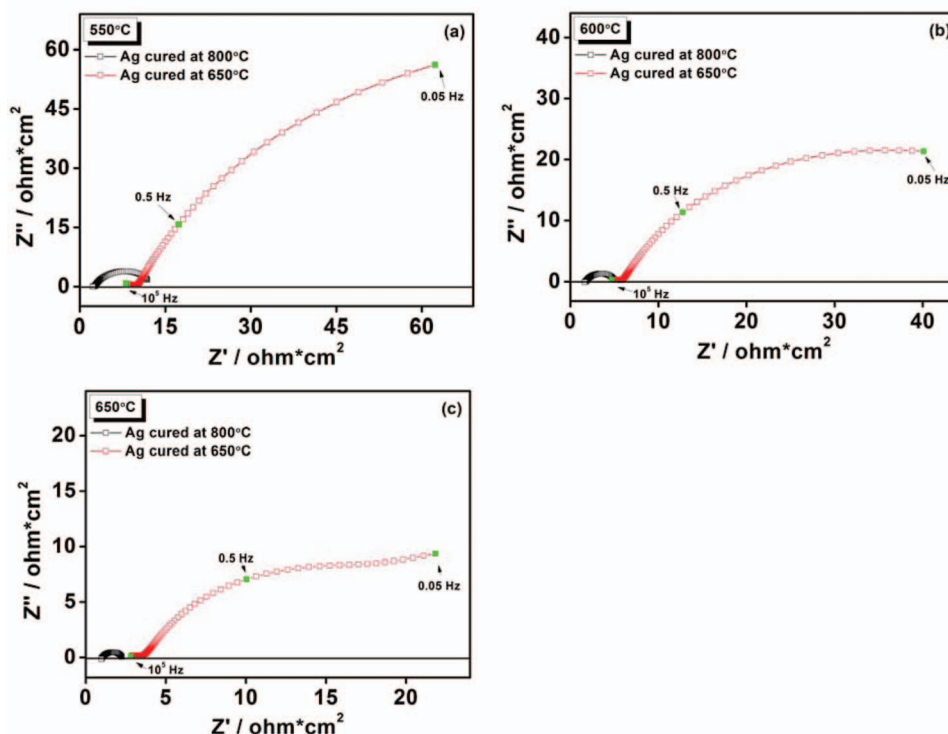


Figure 1. Comparison of impedance spectra of cathode with Ag current collectors cured in situ at 800°C and 650°C.

exhibited a polarization ASR (represented by the arc length of the spectrum on the Z' -axis) at least one order of magnitude lower than that cured at 650°C even though the cell configuration was identical (thickness and area of electrolyte and cathode). Second, the ohmic ASR (represented by the high-frequency intercept with the Z' -axis) of the former cell is also smaller than the latter. These significant differences imply that curing Ag at higher temperature introduced a factor that has promoted the ORR kinetics and electronic conduction. The change in cathode microstructure itself caused by the curing process is unlikely to be the source of the much reduced ASR since the cathode has been pre-calcined at 1100°C prior to the curing of Ag.

In search for the answers to the observations in Fig. 1, we performed SEM/EDS analysis of the cells. Fig. 2a shows the cross-sectional view of the cathode microstructure near the electrolyte/cathode interface after curing Ag at 800°C. Despite the normal microstructure, the compositional EDS analysis in Fig. 2b reveals an abundant and deep distribution of Ag into the cathode microstructure, reaching as far as the electrolyte/cathode interface. As silver can randomly transport via gas phase and/or solid-state diffusion,¹⁰ the resultant distribution of silver phase is not always homogenous, and some agglomerates appear inside the cathode (upper right corner of the Ag-mapping shown in Fig. 2b). Nevertheless, these fine, highly conductive and ORR-active Ag particles have resulted in substantial reduction in polarization ASR observed in Fig. 1. Moreover, the dispersed conductive Ag particles can further decrease the effective ohmic ASR of the LSCF+GDC cathode, thus also lowering the overall ohmic ASR shown in Fig. 1.

In contrast, for the cell with Ag cured at lower temperature 650°C, the migration of Ag from the surface to the bulk of the cathode is absent from EDS analysis (The EDS mapping image was not given as it is a completely dark image), implying that its added promotional effects on ORR kinetics as well as ohmic ASR are limited. Therefore, it is reasonable to believe that the ASRs of LSCF+GDC cathode measured with Ag current collector cured at 650°C is more representative of the true performance of the cathode. For performance evaluation above 650°C, a different current collector is needed. Noble metal Pt

having higher melting temperature and lower vapor pressure is a good candidate.

Another noteworthy observation is the surface morphology of Ag layer coated on the top of LSCF+GDC cathode as shown in Fig. 2c and 2(d). The Ag surface morphology exhibits a relatively dense microstructure of large grains covering the cathode, showing little dependence on the curing temperature. From a gas transport of viewpoint, a dense surface impedes oxygen diffusion.¹⁴ However, the results obtained from this study did not seem to support this common sense. We postulate that the high oxygen solubility ($[O]$) in Ag, not the molecular O_2 transport,²⁰ becomes the primary oxygen source to sustain the ORR during EIS measurements under OCV condition. It could present a problem in real SOFC testing where a greater oxygen flux is required to support a greater cell current.

Pt as a current collector.— To find an appropriate current collector for studies above 650°C, Pt was investigated, the performance of which has been particularly compared with Ag. In this comparative study, Ag and Pt were cured in slightly different heat-treatment conditions: Ag was cured at 800°C in situ while Pt was pre-fired at 950°C. Selection of curing temperature is believed to be important to ensure a good cathode/current-collector bonding and uniform current distribution in cathode microstructure. Higher curing temperature for Pt has been suggested to achieve better electrical contact with the cathode due to its high melting temperature (1773°C). Fig. 3 shows the comparative EIS spectra measured from 700–800°C with Ag and Pt as current collectors. First, it is evident that the polarization ASR of the cell with Ag current collector is appreciably smaller than that with Pt current collector in the entire range of temperatures studied. While lower ASR resulted from Ag current collector is certainly related to the Ag-penetration into the cathode microstructure, higher ASR resulted from Pt current collector implies that the contribution of Pt current collector to the ORR kinetics of the cathode is probably limited, and thus the obtained ASR can be considered a better representative of the true performance of the cathode. Although the obtained polarization ASR of this commercial LSCF+GDC cathode is higher than the result reported by Murray et al.,²² it is better than 100 ohm*cm² at 700°C

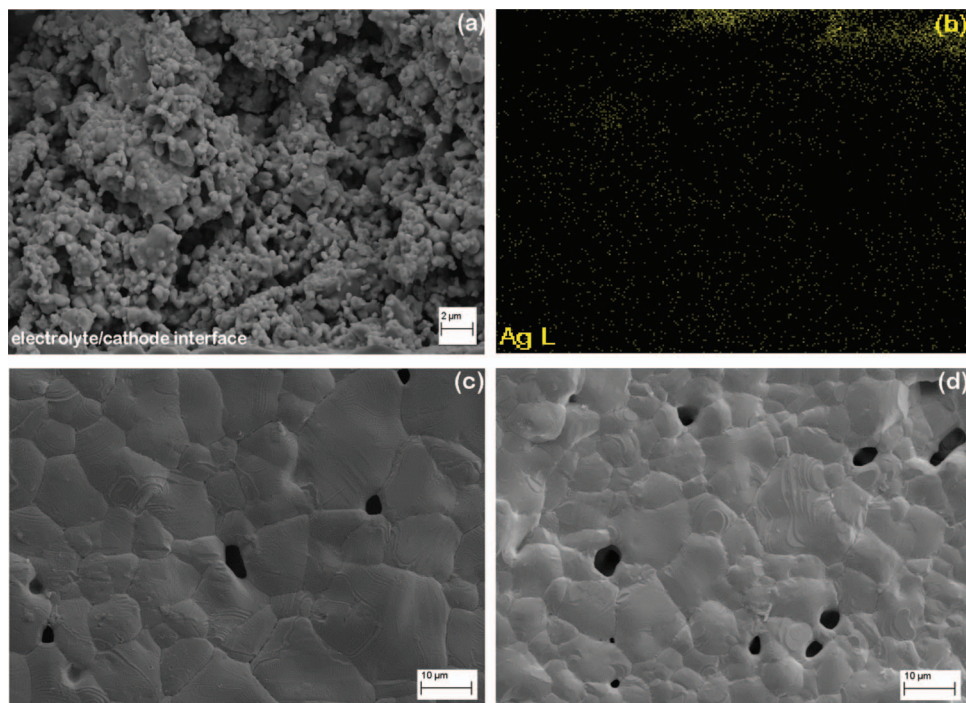


Figure 2. (a) SEM micrographs showing the cross-sectional microstructure of LSCF+GDC cathode with Ag current collector annealed at 800°C; (b) silver distribution across the cathode measured by EDS analysis; (c) Surface morphology of Ag current-collector cured at 800°C; (d) Surface morphology of Ag current-collector cured at 650°C.

obtained from a symmetric cell prepared from the same commercial LSCF paste and Pt mesh current collector.²³ Second, the ohmic resistance of Pt current collector is slightly smaller than that of Ag current collector in spite of its higher polarization ASR. Since the cell properties (geometry and fabrication) are carefully controlled in this experiment, this difference in ohmic ASR is unlikely resulted from

the cell-to-cell variations. One possible reason has been suggested to be related to the use of dielectric frit in commercial Ag paste, making the overall conductivity of Ag paste worse than Pt paste.²⁴

The cross-sectional view and compositional analysis in the cathode/electrolyte interface region of LSCF+GDC cathode with Pt as current collector are shown in Fig. 4a. Other than normal

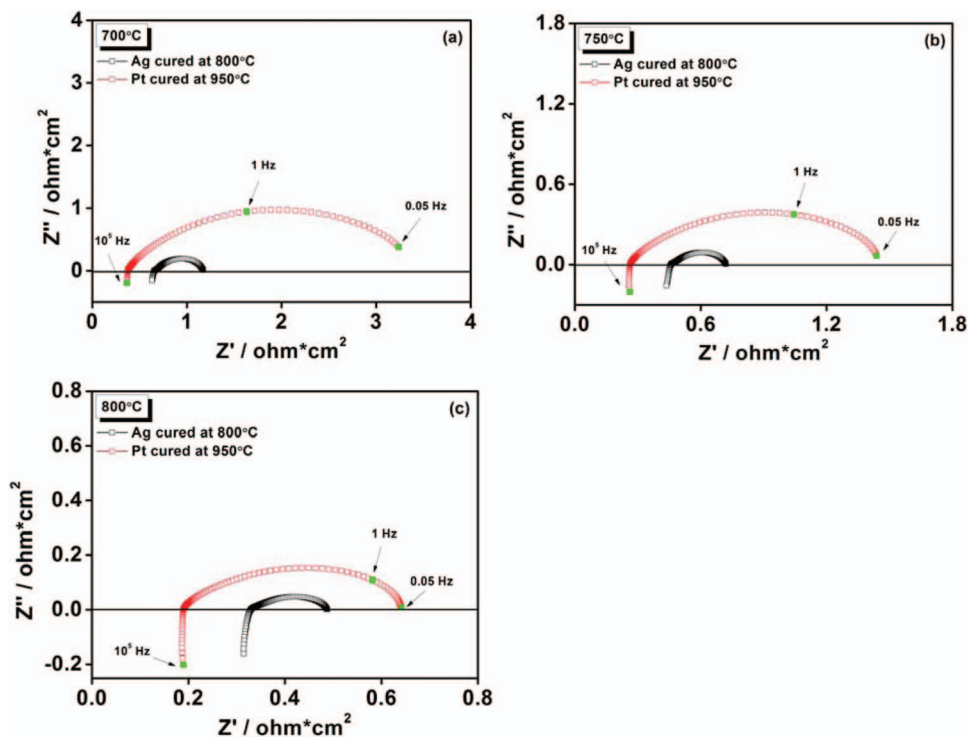


Figure 3. Comparison of EIS spectra of LSCF+GDC/LSGM/LSCF+GDC symmetrical cells with Pt pre-cured at 950°C and Ag cured in situ at 800°C.

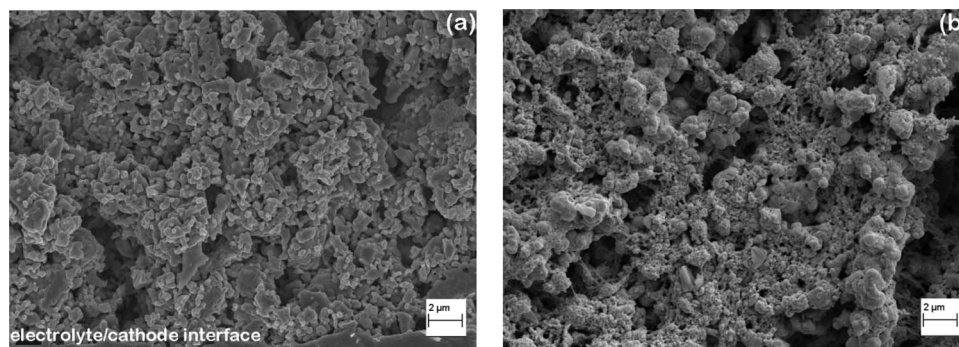


Figure 4. Microstructural analysis of cathode with Pt current collector after impedance test at 800°C: (a) Cross-sectional view of the cathode near the electrolyte/cathode interface; (b) Surface morphology of Pt current collector.

microstructure, no Pt can be detected by EDX (The EDX mapping cannot be shown other than a dark image). Therefore, Pt remains on the surface and should not involve in the ORR kinetics of the cathode under investigation.

An examination of the morphology of the Pt surface in Fig. 4b reveals that it possesses a more porous structure than that of Ag. Although Pt phase and pores are not distributed as uniformly as expected, it is certain that the resultant Pt porous network should provide sufficient pathways for electron conduction and oxygen diffusion.

Conclusions

This study demonstrated that the curing temperature of silver as a current collector in EIS measurements can greatly affect the polarization ASR of a cathode under test. Within a short-term testing time-frame, an EIS symmetrical cell with Ag cured at 800°C exhibited an ASR at least one order of magnitude lower than the same cell with Ag cured at 650°C. Microscopic examination and compositional analysis revealed a deep penetration and abundant distribution of Ag into the cathode/electrolyte interface region. These fine-grained, highly conductive and ORR-active Ag particles/agglomerates were found to be the root cause for the observed substantially lowered polarization and ohmic ASRs. This finding calls for caution when using Ag as a current collector for short-term testing since the involvement of Ag in the ORR kinetics of cathode under investigation could overshadow the true properties of the cathode, thus misleading the conclusions of the study. For long-term effect, the variability of cathode with current collector has been explicitly demonstrated in ref.¹⁰ It was also found that Ag can serve as a more reliable current collector if it is cured and tested at $T \leq 650^\circ\text{C}$. For current collectors working at higher temperatures, Pt is a better choice.

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