Nickel Electrodeposition on Silver for the Development of Solid Oxide Fuel Cell Anodes and Catalytic Membranes

Zadariana Jamil,a,b,c,d Enrique Ruiz-Trejo,a and Nigel P. Brandona

Department of Earth Science and Engineering, Imperial College London, SW7 2AZ, United Kingdom
bFaculty of Civil Engineering, Universiti Teknologi MARA Pahang, Pahang, Malaysia

dberkeley.edu

Nickel was electrodeposited on porous Ag/GDC (silver/Ce0.9Gd0.1O2-x) scaffolds and dense Ag/GDC composites for the fabrication of SOFC electrodes and catalytic membranes respectively. To control the distribution and amount of nickel deposition on the Ag/GDC surfaces: first, a systematic cyclic voltammetry study of nickel electrodeposition from a Watts bath on silver foils was carried out to understand the influence of operating conditions on the electrodeposition process. From the cyclic voltammetry study, it can be concluded that suitable operating conditions for nickel electrodeposition into porous Ag/GDC scaffolds and catalytic membranes are: 1.1 M Ni2+ concentration in Watts bath; deposition potential between −0.65 to −1.0 V vs. Ag/AgCl; a temperature at 55 ºC; sodium dodecyl sulfate (SDS) as the surfactant; pH 4.0 ± 0.2 and an agitation rate of 500 rpm. It was observed that the nickel surface microstructure changed with the deposition current densities due to the co-evolution of H2. Pulse and continuous electrodeposition modes allow nickel to be deposited throughout porous Ag/GDC scaffolds and onto catalytic membranes. The pulse electrodeposition mode is favored as this is shown to result in an even Ni distribution within the porous scaffolds at minimum H2 pitting.

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Nickel is used as a catalyst and current collector in electrochemical energy conversion systems such as solid oxide fuel cells (SOFC’s), electrolyzers, and as a catalyst in catalytic membranes (Figure 1). Conventionally, Ni is incorporated into SOFC anodes by mechanically mixing NiO and ionic conductive materials such as yttria-stabilized zirconia (YSZ) and Ce0.9Gd0.1O2−x (GDC), then sintering at high temperature. However, the use of relatively large volumes of Ni (∼ 30 vol%) needed to achieve adequate electronic conductivity in the electrodes will affect the stability of cell microstructure under high temperature. However, the use of relatively large volumes of Ni (∼ 30 vol%) needed to achieve adequate electronic conductivity in the electrodes will affect the stability of cell microstructure under high-temperature. However, the use of relatively large volumes of Ni (∼ 30 vol%) needed to achieve adequate electronic conductivity in the electrodes will affect the stability of cell microstructure under high-temperature. However, the use of relatively large volumes of Ni (∼ 30 vol%) needed to achieve adequate electronic conductivity in the electrodes will affect the stability of cell microstructure under high-temperature.

Alternative, repeated infiltration involving heating and cooling cycles is a lengthy and energy consuming process, presenting challenges to its industrial application. An alternative is to use electroless and electrodeposition techniques, which offer the potential to accelerate the incorporation of Ni into porous scaffolds at room or near-room temperature. The electroless deposition of Ni is well known and it is a simple process used to coat any substrate, however the use of boron- or phosphorus-based reducing agents in this technique is unsuitable for fuel cells due to adverse catalytic effects of the residues. Alternatively, hydrazine has been used as the reducing agent in the past years, yet its high toxicity may not be suitable for large production. Catalytic membranes have shown their potential to reform methane to syngas (CO + H2) by coupling oxygen separation from air and catalytic partial methane oxidation into one single step. The oxygen is separated from air due to oxygen pressure difference on both sides of dense mixed ionic and electronic conducting (MIEC) membranes such as single phase La1−δSr1−yFe1−xCo1−xO3−δ and/or dual metal-ceramic composites such as Ag/GDC. The incorporation of Ag (< 10 vol %) in dual phase membranes enables oxygen permeability and catalyses oxygen reduction. In previous studies, Ni has been incorporated into the membranes using infiltration techniques or commercial Ni foams. In this study, the electrodeposition of Ni into porous and dense Ag/GDC composites is explored as the process is scalable, low cost and capable of producing Ni deposits with controllable properties. Nickel is deposited into a porous and non-conducting (at room temperature) ceramics such as GDC by combining electroless and electrodeposition: (i) to provide a conductive surface, porous or planar surfaces were metallized with Ag using an electroless technique; and (ii) Ni was electrodeposited on the Ag-coated surfaces using Watts bath. In this work, we report the electrodeposition of Ni on Ag using Watts bath. In particular we aim to:

(i) understand the Ni electrodeposition process on Ag and therefore study Ag foils first;
(ii) find the best condition to deposit Ni deposition on a porous Ag/GDC scaffolds as we are looking for alternatives to the conventional Ni infiltration method to fabricate SOFC electrodes; and
(iii) deposit Ni onto dense Ag/GDC composite membranes to provide catalytic activity for the partial oxidation of methane.

Experimental

Electrolyte for nickel electrodeposition.—The Watts bath was prepared from analytical grade chemicals and deionized water and consisted of 0.86 M NiSO4·6H2O, 0.25 M NiCl2·6H2O and 0.72 M H3BO3 (boric acid). All the experiments were performed at pH 4.0 ± 0.2. The bath was magnetically stirred at 500 rpm to maintain the uniformity of the concentration in the solution and reduce surface pitting. The temperature of the bath was controlled with a hot plate in the range of 22–70 ºC and monitored with a digital thermometer (Leegolal).

Preparation of Ag electrode substrates.—The Ag substrates used as the working electrode (WE) in this study are divided into two groups: planar and porous structures. Figure 2 illustrates the substrate groups, as well as SEM images of the Ag foil and Ag-coated GDC. The substrates were prepared as follows:

(i) Ag foils

Ag foils (0.075mm thickness, 99.97% purity, Figure 2a) were obtained from Advent Research Materials. The working surface area of the foils used in this study was 1cm2 with one side masked by coating with lacquer.

(ii) Ag-coated GDC

Ag coatings (~50 nm thickness) were deposited using Tollens’ method on two different structures: planar GDC electrolytes (Fuel Cell Materials, Figure 2b) and porous GDC scaffolds (Figure 2d). The scaffolds (thickness = ~7–10 µm) were prepared in a similar manner to our previous study.
Figure 1. Principle operation of (a) SOFC; (b) catalytic membranes and (c) solid oxide electrolyser (SOE). The SOFC anode and SOE cathode is a Ni/YSZ or Ni/GDC composite.

Figure 2. The planar and porous substrates group: (a) Ag foil. The SEM image shows the surface of the Ag foil; (b) Ag-coated on GDC electrolyte (planar Ag/GDC); (c) dense Ag/GDC composite membrane; and (d) Ag/GDC scaffold. The SEM image shows a cross section of the Ag/GDC scaffold.

(iii) Dense Ag/GDC composite membranes

The dense planar Ag/GDC membranes (Figure 2c) were prepared by coating suspended GDC powder with Ag using Tollens’ method, then pelletizing the Ag/GDC powder by isostatic pressing and followed by high temperature sintering, as described in previous work.17

Cyclic voltammetry.—The electrochemical experiments were carried out in a three-electrode cell. The WE was silver in the form of either Ag foil, Ag-coated GDC electrolyte, Ag-coated GDC porous scaffold, or a dense Ag/GDC composite membrane. In all experiments, a Ni mesh (99% pure Ni) and silver/silver chloride (Ag/AgCl) were used as counter (CE) and reference (RE) electrodes respectively. Ag foils (area 1 cm²) were used as the substrate to carry out the underpinning study of the electrochemical behavior of Ni electrodeposition on Ag at different bath conditions (temperature, additives, and bath concentrations). Two types of additives were used in this study, a non-ionic surfactant, surfynol (Surfynol 104DPM, Air Products) and an anionic surfactant, sodium dodecyl sulfate (SDS, Sigma-Aldrich). Cyclic voltammetry (CV) was started from the open circuit voltage (OCV), and two potential regions of −1.1 to +0.8 V and −0.9 to +0.8 V were scanned at a scan rate of 5 mV s⁻¹.
Study. Impedance spectroscopy was used to study the electrodeposited symmetrical cell performance from 600 to 750°C in humidified-H2 (97 vol% H2, 3 vol% H2O), in the frequency range of 10−1−106 Hz and with an AC amplitude of 20 mV. Other details follow those described in our previous work.16

Results and Discussion

Typical cyclic voltammetric behavior of Ni on Ag foils.—The typical CVs recorded from OCV to two potential regions, −1.1 to +0.8 V and −0.9 to +0.5 V vs Ag/AgCl are shown in Figure 3. The cathodic current commences at ∼−0.55 V vs Ag/AgCl and a clear current peak (C1 and C1′) appears at ∼−0.65 V vs Ag/AgCl associated with Ni nucleation and reduction in the Watts bath. The equilibrium Ni2+ reduction potential (E°Ni2+/Ni0 at 55°C, 1.1 M NiCl2), is ∼−0.47 V vs Ag/AgCl, with the offset probably due to a nucleation barrier.21,22 Then the current increases sharply when the scan proceeds toward more negative potentials (>−0.75 V vs Ag/AgCl) for both overpotential ranges, corresponding to nickel deposition with metallic gray deposits and co-evolution of H2. The co-evolution of H2 became visible with the formation of H2 gas bubbles at the edges of the deposited layer on the WE (Ag foil) beyond −1.0 V vs Ag/AgCl (Figure 3a). It is reported that adsorbed hydrogen molecules (Hads) are strongly bonded on the surface of fresh Ni deposits and form Ni-hydrogen alloys, inhibiting the growth of Ni.23−25 In some cases, the continuous co-evolution of H2 bubbles led to delamination of the deposited layer from the Ag foil.

On the reverse potential scan, in the positive direction, a crossover point when the current becomes almost zero is observed, indicating that the nickel electrodeposition proceeds through nucleation and growth phenomena.26,27 On scanning to more positive potentials, anodic peaks corresponding to oxidation reactions were observed. The existence of Ni-hydrogen alloys is shown by two anodic peaks (a1 and a2) at ∼+0.1 V and ∼+0.2 V (Figure 3b), associated with the dissolution of two separate phases, α-Ni (solid solution of hydrogen in Ni, H/Ni ∼0.3) and β-Ni (H/Ni > 0.6).28−30 These peaks are clearly formed when a narrower potential window is used, indicating a mixture of two phases of Ni-hydrogen alloy and pure Ni are deposited in the early stages of Ni deposition. When a broader potential window is used (Figure 3a), the anodic peaks appear at ∼+0.2 V (a1) followed by the peak at ∼+0.3 V (a2) and ∼+0.75 V (a3), indicating the dissolution of β-Ni and Ni metal, and oxidation of Ni species (hydroxide/oxide) respectively.31,32 This shows that β-Ni is primarily formed when a higher negative potential is applied (∼−1.0 V vs Ag/AgCl) compared to α-Ni.33 The oxidation of Ni species to hydroxide/oxide was observed by the formation of a black deposited layer. The black layer remained when scanned for the second and third cycles. This might be an indication as to the source of deactivation or inhibition of the subsequent electrodeposition on the electrode.34,35 The overall Ni redox reactions from a Watts bath at cathodic and anodic regions are summarized in Table I.

Cyclic voltammetry at different operating conditions.—A systematic cyclic voltammetry study of the influence of operating conditions on Ni deposition on Ag foils is shown in Figure 4. All voltammograms scanned from OCV to several potential regions of −1.1 to +0.9 V, −1.1 to +0.8 V and −0.9 to +0.5 V vs Ag/AgCl.

Effect of Ni2+ concentration.—Figure 4a shows the influence of Ni content in the Watts bath on the deposition of Ni on Ag foils (at pH ∼4, 500 rpm and T = 55°C). The current densities in boric acid (0.72 M) were very low (∼−0.7 mA cm−2 at −1.0 V vs Ag/AgCl), showing minimal reaction occurred. This was confirmed by visual observation during the voltammetry cycle (no change of the Ag surface). Decreasing of Ni2+ concentration in the Watts bath from 1.1 to 0.01 M shifted the Ni2+ reduction potential to more negative values by 0.2 V (−0.75 to −0.95 V vs Ag/AgCl). This may be attributed to an increase of concentration and activation overpotentials.36,37 At higher Ni2+ concentrations, a rapid rise in current density is observed toward
Table I. Possible cathodic and anodic reactions during cyclic voltammetry in Watts bath.

| Redox Reactions | Potential, V vs Ag/AgCl |
|-----------------|-------------------------|
| **Cathodic reactions** | |
| Deposition of Ni on the WE: | Ni^{2+} + 2e^- ↔ Ni | ~0.65 |
| Deposition of α- or β-Ni: | Ni + H_2O + 2e^- ↔ Ni-H included (α or β) + OH^- | >~0.65 |
| Co-evolution of H_2: | 2H^+ + 2e^- ↔ H_2 | ~0.44 |
| **Anodic reactions** | |
| Dissolution of α- and β-Ni: | Ni-H included (α or β) + OH^- ↔ Ni^{2+} | ~+0.1 V/~0.2 V |
| Oxidation of Ni to Ni^{2+}: | Ni ↔ Ni^{2+} + 2e^- | ~+0.3 |
| Oxidation of Ni to Ni(OH)_2 and NiO: | Ni + 2OH^- ↔ β-Ni(OH)_2 | >+0.75 V |

Negative potentials as a result of the increase of electroactive species in the Watts bath. Thus, better deposits are expected at higher Ni^{2+} concentrations. To minimize mass transport limitations and to obtain satisfactory Ni deposits, a Ni^{2+} concentration of 1.1 M was selected for the subsequent deposition studies.

**Effect of bath temperature.**—Figure 4b shows that the Ni reduction potentials shifted to less negative values, from ~0.75 to ~0.64 V vs Ag/AgCl when the bath temperature increased from 22 to 70 °C. An increase of temperature may decrease the overpotential of both H_2 evolution and nickel reduction. However, high plating temperatures lead to hydrolysis reactions that leads to the inclusion of impurities in the deposited films such as nickel hydride and develop internal stress within the deposits. Consequently, the deposits may form cracked and poor coatings. Therefore a temperature at 55 °C was chosen for the next deposition process.

**Effect of additives.**—The effect of non-anionic (surlynol) and anionic (SDS) additives in the Watts bath are illustrated in Figure 4c. The addition of SDS causes the deposition overpotential to shift to more negative values, and decreases the peak current density from ~0.13 to ~0.10 A cm^-2 at ~1.1 V vs Ag/AgCl compared to surfynol. Figure 5 depicts Ni layers deposited at continuous potential over time on Ag foil with the addition of SDS and surfynol. The addition of SDS further decreases the peak current density compared to surfynol.

![Figure 4](image-url) Volammograms showing the effect of operating conditions on Ni electrodeposition on Ag foils at a scan rate 50 mV s^-1 within potential windows of ~1.1 to +0.9 V, ~1.1 to +0.8 V and ~0.9 to +0.5 V vs Ag/AgCl as a function of (a) Ni concentration in Watts bath; (b) temperature; (c) additives and (d) Ag substrates.
of SDS into Watts solution significantly reduced H₂ pitting compared to surfynol. A compact and brighter Ni layer formed with SDS (Figure 5a), however, a darker layer of Ni accompanied by some sub-micron pores due to H₂ evolution was obtained with surfynol (Figure 5b). This shows that SDS is favored as it enhances the electrostatic adsorption of Ni²⁺ ions by increasing their positive charges, and suppressing H₂ evolution.²⁷

**Effect of substrate structure.—**Different Ag substrates (Ag/GDC scaffolds, planar Ag/GDC and Ag/GDC composite membrane) were used to elucidate the influence of substrate structure on the nickel electrodeposition process as ultimately we want to deposit nickel onto these substrates for a range of applications. Figure 4d shows the cathodic region of the cyclic voltammograms of Ni deposition on the different substrates in the Watts bath. The voltammograms of Ni deposition on the planar Ag/GDC, Ag/GDC scaffold, and Ag/GDC composite membrane, follow the same trends as seen on Ag foil, showing the presence of a similar charge controlled process. A cathodic wave (C) at −0.7 V vs Ag/AgCl for Ni deposition on the porous Ag/GDC scaffold is clearly observed. This peak may indicate that the deposition of Ni in the porous scaffold may involve a combination of charge and diffusion controlled processes with co-evolution of H₂.³⁹,⁴⁰ Furthermore, it is observed that the current densities for the Ag/GDC scaffold, planar Ag/GDC and Ag/GDC composite membrane are smaller than that obtained on the flat Ag foil, despite their increased surface area. These observations could be due to a combination of:

(i) non ideal current distribution on the Ag-coated GDC and Ag/GDC membrane surfaces; and
(ii) mass transport limitations related to the diffusion of Ni²⁺ ions through the porous support to the metal-electrolyte interface.³¹,⁴²

A narrow range of applied potentials was selected to deposit Ni, particularly in the porous structures to minimize the co-evolution of H₂ that can otherwise interfere with the growth and structure of Ni deposits. The operating conditions selected for Ni electrodeposition into porous Ag/GDC scaffolds and onto Ag/GDC membranes were: 1.1 M Ni²⁺ concentration in the Watts bath; potential range between −0.65 to −1.0 V vs. Ag/AgCl; temperature 55°C; SDS as the surfactant; pH 4.0 ± 0.2 and agitation rate 500 rpm.

**Structural and morphological properties.—**Characterization of Ni electrodeposition on Ag foil.—XRD and EDX measurements confirmed the presence of Ni for all deposition regimes from low to high current densities (within the range of −0.65 to −2.5 V). Figure 6 compares X-ray diffractograms of Ni electrodeposited films on Ag foils using a pulse current of −0.008 to −0.83 A cm⁻². The XRD data were normalized to the highest intensity of Ag foil as the reference. As expected, all Ni electrodeposited films were found to be pure Ni with no peaks of other phases observed. The Ni electrodeposits with strong orientation along the (111) direction (ICSD No. 064989) at lower current densities (<−0.2 A cm⁻²) changed to the (200) and (220) directions at higher current density. This might be attributed to the existence or formation of different interfacial inhibitors such as H₂, H₂ ads or Ni (OH)₂ at the nickel-electrolyte interface during the deposition process.³⁴,³⁵⁻⁴⁵

Figure 7 shows a series of SEM micrographs of Ni films electrodeposited on Ag foil prepared using pulse current plating at different current densities. The surface morphology of Ni deposits changed from fine grains to pyramidal-shaped growth and then cauliflower-shaped morphology when the current densities increased from −0.008 to −0.83 A cm⁻². The low current densities led to very slow growth rates of Ni. This suggests that fine Ni grains form and accumulate in the early stage of Ni electrodeposition. The high current densities contributed to excess co-evolution of H₂ that caused defects in the Ni films (Figure 8a) and even delamination of the films from the substrate. Ni dendrites were seen on the cauliflower-like Ni films at higher current densities (Figure 8b), accompanied by hydrogen evolution. For these reasons, the deposition of Ni at high current density is not recommended. From elemental analysis of the total Ni deposited dissolved in aqua regia, a current efficiency of ~90% was found in the range of −0.008 to −0.08 A cm⁻² (~0.65 to −1.0 V vs Ag/AgCl).

**Nickel deposition using different electrodeposition modes (CED and PED).—**Ni electrodeposition on Ag/GDC scaffolds was conducted using chronoamperometry at −0.8 V vs. Ag/AgCl. The deposition was conducted in direct and pulse mode for 69 s (total applied voltage time). The pulse off-time and on-time were 400 ms and 900 ms respectively. Figure 9 shows the elemental distribution mapping of Ni deposited at −0.8 V in both CED and PED modes. Both deposition modes enable Ni deposition throughout the porous scaffold, but when using CED mode more Ni is observed deposited on the top of the porous scaffold (Figure 9b). This layer can block the transport of Ni²⁺ into the innermost pores where the local ion concentration can then be depleted. However, Ni deposits at the top of the scaffold using PED mode (Figure 9a) were less evident than in CED mode. Furthermore, the distribution of Ni was more homogenous and dense in the pores. This suggests that during the off-time, the open pores at the top of the scaffold allow the diffusion of Ni²⁺ back into the pores.³⁹,⁴⁰ Since our interests are to engineer and control the Ni microstructures in Ag/GDC scaffolds as the anodes of SOFCs, PED mode of electrodeposition is preferable in order to minimize the blocking pores on the top of scaffolds. However, in the case of catalytic membranes, either PED or CED can be used to deposit Ni layers onto the dense and planar Ag/GDC.

**Electrochemical characterization of Ni/Ag/GDC symmetrical cell.—**An electrodeposited Ni/Ag/GDC symmetrical cell with composition of 11.3/14.8/73.9 wt% was prepared using the
Figure 7. Influence of current density on the surface morphology of Ni on Ag foils during pulsed deposition ($T_{\text{off}} = 900$ ms and $T_{\text{on}} = 400$ ms, 240 cycles) at (a) $-0.008$ A cm$^{-2}$; (b) $-0.01$ A cm$^{-2}$; (c) $-0.04$ A cm$^{-2}$; (d) $-0.08$ A cm$^{-2}$; (e) $-0.2$ A cm$^{-2}$; (f) $-0.5$ A cm$^{-2}$ and (g) $-0.83$ A cm$^{-2}$. The inset figures are the optical images of the deposited Ag foils where the circular spot indicates the place where silver coil was connected.

electrodeposition conditions identified from the CV study. The electrochemical performance of this symmetrical cell was measured and characterized. Figure 10a shows the impedance response of the symmetrical cell operating at 600–750 $^\circ$C in humidified-H$_2$ (97 vol% H$_2$, 3 vol% H$_2$O) over the frequency range of $10^{1}$–$10^{6}$ Hz. These impedance spectra were fitted using the equivalent circuit shown in Figure 10b to estimate polarization resistance values of the cell. Two semicircles were observed, indicating the polarization of the cell at high, intermediate and low frequencies. The intercept of the impedance spectra at high frequencies with the real axis corresponds to the ohmic resistance ($R_{\text{ohm}}$). The difference between the low frequency intercept of the impedance curve with the real axis and the $R_{\text{ohm}}$ gives the total area specific resistance (ASR) of the electrode. These values were extracted from the fitting and then normalized by dividing by two and multiplying by the electrode area (1.15 cm$^2$).

$R_{\text{ohm}}$ decreases when the temperature increases, indicating that it is primarily related to the ionic conductivity of the electrolyte. The ASR of the electrode (inset table in Figure 10), including polarization resistance at intermediate ($R_{\text{m}}$) and low ($R_{\text{l}}$) frequencies, was significantly decreased from 2.31 to 0.57 $\Omega$ cm$^{-2}$ when the temperature increased to 750 $^\circ$C. The lowest ASR obtained in this study was 0.57 $\Omega$ cm$^{-2}$, approximately half the value reported in our previous study (1.12 $\Omega$ cm$^{-2}$), fabricated using a similar GDC scaffold. This result indicates that the identified electrodeposition conditions used for depositing Ni onto Ag/GDC scaffold improved the performance of the anode, though the value remains greater than data reported in the literature for Ni/GDC and Ni/YSZ anodes fabricated using conventional and infiltration techniques (0.1–0.35 $\Omega$ cm$^{-2}$), showing that more optimization is needed to further improve performance, and in this regard many process variables remain to be explored.

Conclusions

The influence of the operating conditions of a Watts bath for Ni electrodeposition on Ag foils using CV has been investigated. Ni started to electrodeposited on Ag substrates at $\sim -0.65$ V vs Ag/AgCl. More negative potentials allowed faster growth of Ni, however this led to the co-evolution of H$_2$ ($\geq -1.0$ V vs Ag/AgCl). The co-evolution of H$_2$ in large amounts resulted in defects in the deposited layers due to H$_2$ voids. Nickel dendrites and delamination of the layers from the substrate were also observed as current density increased.

The suitable electrodeposition conditions were identified to be 1.1 M Ni$^{2+}$ in the Watts bath; a potential range of $-0.65$ to $-0.95$ V vs Ag/AgCl; temperature 55 $^\circ$C; SDS as the surfactant; pH 4.0 $\pm$ 0.2
and agitation rate at 500 rpm; to maximize the deposition of Ni into porous Ag/GDC scaffolds and membranes. SDS was selected as the additive because it limited the co-evolution of H₂, and produced a compact, homogeneous and bright coating. Ni deposition using PED within the suggested potential range was shown to be preferential due to its ability to (i) deposit evenly in the pores; (ii) reduce the potential for pore blockage on the top of porous scaffolds; and (iii) allow the transport of Ni²⁺ into the electrode region during the off period. In the case of partial oxidation membranes, both CED and PED can be used to deposit Ni layers on dense Ag/GDC substrates. The electrochemical performance of the electrode produced using the identified conditions improved from a previous study, 1.12 Ω cm⁻²,¹⁰ to 0.57 Ω cm⁻² in this study at 750°C in humidified-H₂ (97 vol% H₂, 3 vol% H₂O).

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