Robust SOFC Anode Materials with La-Doped SrTiO₃ Backbone Structure

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Redox-stable Sr_{0.9}La_{0.1}TiO₃ (SLT) with Ce_{0.9}Gd_{0.1}O₂ (GDC) and (Sc₂O₃)_{0.1}(CeO₂)_{0.01}(ZrO₂)_{0.89} (SSZ) was used to fabricate robust anodes for zirconia-based electrolyte-supported SOFCs. The anode consisted of three layers: a layer of 60wt% GDC-40wt% SLT or 40wt% SSZ-60wt% SLT as a functional layer and two layers of SLT as current conducting layers. An impregnation method has been employed to decorate nano-sized Ni and CeO₂ into the ceramic anode to improve electrochemical performance and redox stability. It was found that the catalyst impregnated ceramic anode has improved redox stability compared with the conventional Ni-SSZ cermet. The incorporation of the oxide catalyst, CeO₂, during co-impregnation process was found to even further improve redox stability of the anode, since CeO₂ particles have a lower tendency to aggregate during redox cycling.

A part of this study has been presented in SOFC-XIV in Glasgow UK, and appeared in *ECS Transactions*, Vol. **68** (1) 1447 (2015).

Keywords:

Solid oxide fuel cell

La-doped SrTiO₃ oxide anode

Ni-CeO₂ co-impregnation

Redox stability

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1. Introduction

Solid oxide fuel cells (SOFCs) are electrochemical energy conversion devices that can directly produce electricity from fuel, which avoids the intermediate energy conversion losses and achieve much higher electric efficiency. Porous Ni- yttrium-stabilized zirconia (YSZ) cermet has been used as the state of the art SOFC anode for decades because of its high electrochemical and catalytic activities and low cost. In the cermet composite, the Ni metal phase provides the required electronic transport pathway and catalytic activity, whereas the YSZ ceramic phase lowers the coefficient of thermal expansion for the anode to match that of the electrolyte, prevents the Ni phase from coarsening, and offers a conduction pathway for oxygen ions and thus extends the active zones for anode reactions [1]. To achieve sufficient current collection and catalytic activity, the nickel content is usually over 35 vol. % to form a connecting path for electron transport. However, nickel in the anode would be reoxidized in a commercial SOFC system in situations such as seal leakage, fuel supply failure, system shutdown, and possibly even very high fuel utilization. Thus reduction and oxidation (redox) cycling of the anode is likely to occur during commercial SOFC system operation. The reduction and oxidation of Ni will cause large volume changes, which could lead to fracture either of the anode itself or of its adjacent components, e.g. thin electrolyte [2, 3]. Even though the latest fundamental studies indicated that electrical properties could be enhanced through large mechanical strains [4-8], thermal expansion or chemical expansion mismatches should be limited to a reasonable magnitude considering the balance between both excellent electrical properties and long-term stability.

Therefore, it is desirable to develop alternative anode materials with high thermal compatibility, sufficient redox stability, and comparable electrochemical performance as that of

the Ni-YSZ cermet. Oxide anodes [have received substantial](#) attention for [many](#) years, [including](#) perovskite materials such as doped LaCrO_3 and doped SrTiO_3 , and the double perovskite materials such as [Sr₂Mg_{1-x}Mo_xO_{6-δ}](#) [9]. However, the electronic conductivity of doped LaCrO_3 is only on the order of 1 Scm^{-1} under SOFC anode conditions [9]. [Crucially](#), the double perovskites [are not stable](#) with YSZ [10]. Marina [et al.](#) [11] and Wang [et al.](#) [12] thoroughly evaluated the electrical and thermo-mechanical properties of $\text{Sr}_{1-x}\text{La}_x\text{TiO}_3$ as a possible SOFC interconnect material. According to the Wang et al., the air-sintered 10% La-doped SrTiO_3 has a thermal expansion coefficient (TEC) of $11 \times 10^{-6} / ^\circ\text{C}$ and an acceptable electrical conductivity ($>13 \text{ S/cm}$) under the SOFC anode condition. In addition, the air-sintered $\text{Sr}_{0.9}\text{La}_{0.1}\text{TiO}_3$ shows negligible linear expansion in the cyclic redox test. In this study, we utilize the redox-stable $\text{Sr}_{0.9}\text{La}_{0.1}\text{TiO}_3$ to fabricate robust SOFC anodes. To compensate the insufficient ionic conductivity of the $\text{Sr}_{0.9}\text{La}_{0.1}\text{TiO}_3$, SSZ or GDC will be introduced as the ionic conducting phase. Moreover, a very small amount of Ni and CeO_2 is homogeneously impregnated onto the ceramic anode surface to provide catalytic activity and to avoid structural fracture during the redox cycling.

2. Experimental

2.1. Cell fabrication.

Scandia-stabilized zirconia (SSZ) plates (10 mol% Sc_2O_3 - 1 mol% CeO_2 - 89 mol% ZrO_2 , Daiichi Kigenso Kagaku Kogyo Co., Ltd., Osaka, Japan) with a diameter of 20 mm and a thickness of 200 μm were used as solid electrolytes. $\text{Sr}_{0.9}\text{La}_{0.1}\text{TiO}_3$ (Praxair, Inc., Connecticut, US) powder was mixed with SSZ or GDC in 20 wt%, 40 wt%, 60 wt%, and 80 wt%. The composite powders were then homogeneously blended with organic binder (α -terpineol) as the different anode functional layer pastes. 50 wt% LSM (Praxair, Inc., Connecticut, US) powder was blended with SSZ in the binder as the cathode functional layer paste. The anode current collecting paste and the cathode current collecting paste were prepared by mixing binder with SLT and LSM, respectively. The anode functional layer (30 μm in thickness, 0.64 cm^2 in area) was screen printed on the electrolyte. After drying, the second and the third $\sim 30 \mu\text{m}$ SLT current collecting layers were printed using same SLT slurry, followed by sintering in air at 1300 $^\circ\text{C}$ for 3 h to ensure a good current-collecting structure. The LSM-SSZ (50-50) composite functional layer and the LSM conducting layer were then screen printed on the counter side of the SSZ electrolyte plate, followed by sintering in air at 1200 $^\circ\text{C}$ for 5 h. The cell configuration is illustrated in Figure 1 (a).

For the impregnation, the prepared porous anode layer was impregnated with an aqueous solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ or a mixture of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ followed by thermal decomposition at 800 $^\circ\text{C}$ in air to obtain 10wt% Ni impregnated SLT cermet (Ni/SLT cermet), 20wt% Ni impregnated SLT cermet (Ni/SLT cermet), or 10wt% Ni-10wt% CeO_2 co-

impregnated SLT cermet (Ni-CeO₂/SLT cermet). The weight gain (calculated from Ni or CeO₂ particles) in each impregnated step was 2.5 wt% (0.23mg). Four or eight repetitions were performed to achieve either 10 wt% or 20 wt% weight gain, respectively. A schematic illustration of the nano-catalysts impregnated oxide anode is shown in Figure 1 (b). Pt mesh was attached to each electrode surface as a current collector using SLT or LSM slurry as paste avoiding any contact between Pt mesh and electrode functional layers. Pt paste was used as a reference electrode (RE) located more than 2 mm away from the edge of the cathode [13, 14].

2.2. Cell test

To measure the electrochemical performance, the single button cell was sandwiched by two alumina rings and sealed by ceramic binder, before being attached to alumina tubes and sealed with a glass sealant. The cell was tested at 800°C with 100 ml min⁻¹ 3%-humidified H₂ as the fuel and 100 ml min⁻¹ air as the oxidant. Prior to the cell testing, the anode was exposed to a hydrogen atmosphere at 900°C for 5 h to reduce the NiO to Ni. The cell performance was evaluated by a Fuel Cell Test Station (Toyo Corp.). The voltage loss on the anode side was obtained by comparing the potential difference between the anode and the reference electrode (on the cathode side) with the open circuit voltage. The anode-side voltage loss was then divided into the anodic polarization and the anode-side ohmic loss using the well-known current interruption technique. These non-ohmic and ohmic contributions were experimentally separated by regularly monitoring the voltage relaxation at 15 μs, just after the current interruption [14]. Within 15 μs, the ohmic voltage loss due to the ionic and electronic conduction should effectively be relaxed [15]. Most of the (non-ohmic) electrode processes have a longer relaxation time, i.e., lower relaxation frequencies [15]. Note that the non-ohmic anodic polarization may consist of an

activation polarization and a concentration polarization, the separation of which may be possible in a future study, by applying impedance [spectroscopy](#) analysis. [The](#) microstructure of the anodes was observed by a scanning electron microscope (SEM).

2.3. Redox cycling test.

The redox stability test was performed based on the SOFC shutdown protocol for real SOFC systems published previously [16]. In this protocol, the fuel supply shuts off and the temperature changes very [quickly](#). [The](#) cell is cooled down to 400°C in 1h, and then maintained at 400°C for 30 min. The cell [is](#) then heated to 800°C in 1h, and [held at that temperature for a further 1h](#). Fuel [is](#) supplied during heating and power generation, [and](#) stopped during cooling and at the lowest temperature. After each cycle, the temperature [is](#) maintained at 800°C, and the cell voltage [is](#) measured at a constant current density (0.2 Acm⁻²) [16]. In the current experiments, [we utilized](#) the fuel interruption based on the shutdown protocol to perform redox cycle and kept the cell at [a](#) constant temperature of 800 °C, while other parameters [remained the same as with](#) the shutdown protocol.

3. Results and discussion

3.1. SLT oxide anode backbone

Figure 2 (a) and (c) illustrate the anode-side ohmic loss and anodic overpotential of the SOFC single cells using a SSZ-SLT oxide anode in different compositions. It was observed that the anode-side voltage loss mainly came from the anodic overpotential indicating the insufficient electrocatalytic activity. The 40wt%SSZ-SLT (denoted as S40) was found as the optimized composition with the lowest anodic overpotential. In the case of the GDC-SLT group, the anode-side ohmic loss and anodic overpotential of the cells using the GDC-SLT oxide anode in different compositions are illustrated in Figure 2 (b) and (d). The 60wt%GDC-SLT (denoted as G60) was found as the optimized composition with the lowest anodic overpotential. In addition, the GDC-SLT group was found to reduce anode-side ohmic loss and anodic overpotential compared to that of SSZ-SLT group. A reason for this may be because of the mixed ionic-electronic conducting property and catalytic activity of GDC in reducing atmosphere [21, 22].

3.2. I-V measurement

Figure 3 (a) represents the I-V curve of SOFC single cells using the S40 backbone anode (without catalyst), the 10wt% Ni impregnated S40 anode, and the 10wt% Ni-10wt% CeO₂ co-impregnated S40 anode. The maximum power density increased from an initial 17.1 mWcm⁻² to 344.3 mWcm⁻² and 651.7 mWcm⁻² after Ni and the mixture of Ni and CeO₂ were impregnated onto the S40 backbone, respectively. The anodic polarization significantly decreased as the

catalyst was impregnated, which provides direct evidence of the catalyst improving the performance, as shown in Figure 3 (b).

A similar trend could be observed in Figure 4 (a) for I-V curve of SOFC single cells using the G60 backbone anode (without catalyst), the 10wt% Ni impregnated G60 anode, and the 10wt% Ni-10wt% CeO₂ co-impregnated G60 anode. The initial cell with the G60 backbone anode achieved fairly poor performance with a maximum power density of 118.4 mWcm⁻². With the nano-Ni impregnation or the simultaneous Ni-CeO₂ co-impregnation, the anodic polarization further reduced and cell performance remarkably improved to 542.8 mWcm⁻² and 764.8 mWcm⁻², respectively.

3.3. Redox stability

We have investigated redox stability of the 10wt% Ni-10wt% CeO₂ co-impregnated G60 and S40 anodes by reducing and oxidizing the anodes cyclically 50 times. The same redox cycling test was also performed for the Ni-SSZ anode [11] and the single-phase 20wt% Ni impregnated G60 anode. Terminal voltage patterns of single cells using the 20wt% Ni impregnated G60 anode, the 10wt% Ni-10wt% CeO₂ co-impregnated G60 anode, and the 10wt% Ni-10wt% CeO₂ co-impregnated S40 anode during the first 10 redox cycles are shown in Figure 5 (a), (b), and (c), respectively. Cells stably operated at 200 mAcm⁻² for 1 h when the anode was exposed to hydrogen. Then, the cell voltages gradually dropped to 0 V within the first 10 min when the current loading and fuel supply were shut off for 1.5 h during which the anode was exposed to the oxidizing atmosphere with same oxygen partial pressure as cathode side. Finally, current loading was restarted after supplying fuel to the anode chamber for another 1 h to finish one redox cycle. During the fuel shut-off, the oxidizing atmosphere in the anode chamber was

induced by the high temperature air diffusion through the glass sealing, which simulated the real situation of SOFC systems during emergent fuel shut-off [16].

The average voltage under the current loading was measured every cycle, and it was found that cell performance severely deteriorated 6.8% in 10 redox cycles when the 20wt% Ni impregnated G60 anode was employed. A significant redox stability improvement was found when Ni was partially substituted by CeO₂ by co-impregnation. The cell performance dropped only 0.52% in voltage for the 10wt% Ni-10wt% CeO₂ co-impregnated G60 anode, and 0.45% for the 10wt% Ni-10wt% CeO₂ co-impregnated S40 anode. All the impregnated anodes exhibited better redox stability than the conventional Ni-SSZ cermet as we have studied previously, the cell performance of which dropped by 7.5% in 10 redox cycles and by 23% in 50 redox cycles [16].

Anode-side ohmic loss and anodic polarization were separated during the entire 50 cycles. Figure 6 (a) and (b) illustrate the anode-side ohmic loss and the anodic polarization of three different anodes during redox cycling. Ohmic loss of all the impregnated anodes remained stable at a very low level. However, the anodic polarization of the 10wt% Ni-10wt% CeO₂ co-impregnated anode increased only slightly, whereas the anodic polarization of the 20wt% Ni impregnated G60 anode dramatically increased in the first 10 redox cycles and then slowly increased for the remaining 40 cycles.

3.4. Cell performance after redox cycling test

The I-V curve of the SOFC single cells using three different anodes before and after the redox cycling test is shown in Figure 7. The use of the 20wt% Ni impregnated G60 anode achieved the highest performance among all these different anodes, however, the cell shows significant

degradation as the current density [was](#) increased, which implied that the cell performance also deteriorated more [severely](#) for the high current density region as shown in Figure 7.

The 50wt% partial substitution of CeO₂ [in the impregnated catalysts](#) slightly reduced the cell performance compared with the same amount of pure Ni impregnation, nevertheless, it effectively promoted performance stability against redox cycling. In the low current density region, the I-V curves did not show much difference before and after the redox cycling test. As the current density increased, the voltage difference gradually increased but [less so than](#) that in the case of the pure Ni impregnation. In Figure 7 (b) and (c), the same amount of Ni and CeO₂ was impregnated into the anode as a catalyst, as described earlier. The 10wt% Ni-10wt% CeO₂ co-impregnated G60 anode demonstrated better performance than the 10wt% Ni-10wt% CeO₂ co-impregnated S40 anode, whereas it deteriorated slightly more at the constant current of 200 mAcm⁻² even though they both generally exhibited excellent stability against redox cycling.

We calculated the degradation [rates of the cells](#) performance at [a](#) constant current density of 200 mAcm⁻² in the first 10 cycles and the entire 50 [cycles](#). We found that, when using the 20wt% Ni impregnated G60 anode, cell performance degraded around 6.8% in the first 10 redox cycles, and 11% in the entire 50 redox cycles as shown in Figure 8. [It has already been](#) shown in Figure 6 that anodic polarization of the 20wt% Ni impregnated G60 anode [increased comparatively](#) faster in the initial stage, whilst its ohmic loss [maintained a](#) very low level during the entire 50 redox cycles. The partial substitution of CeO₂ suppressed the initial stage degradation of anodic polarization, but long-term degradation was slightly accelerated probably due to catalyst sintering.

3.5. Microstructural change after redox cycling test

Our previous study systemically investigated the microstructural change of Ni-SSZ anodes

against redox cycling, and found a decrease in the amount of Ni near the anode triple-phase-boundary (TPB) and Ni grain coarsening near the anode surface [16]. In this study, we analyzed the microstructural change of the impregnated anode before and after the redox cycling test as shown in Figure 9. Figure 9 (a) and (b) show the microstructural change of the 20wt% Ni impregnated G60 anode before and after the redox cycling test. The nano-sized Ni particles were randomly distributed with a relatively small particle size (50~100 nm) before the redox cycling test, while the distribution of the nano-Ni particles significantly changed after the 50 redox cycles. [Substantial](#) nano-Ni aggregation is clearly distinguished in Figure 9 (b), and the large aggregated islands were formed by agglomeration of small particles.

Figure 9 (c) and (d) represent the case of the 10wt% Ni-10wt% CeO₂ co-impregnated G60 anode. The randomly distributed particles were hardly differentiated before the redox cycling test, but the Ni phase and the CeO₂ phase were clearly separated after the redox cycling test. Ni particles grew and aggregated into large isolated particles. CeO₂ particles also [aggregated slightly](#) into connected networks covering the ceramic [surface, but](#) did not further grow into large isolated particles as that of the Ni phase. [The](#) 10wt% Ni-10wt% CeO₂ co-impregnated S40 anode was similar as that of the co-impregnated G60 anode: Ni groups grew and CeO₂ groups slightly connected as shown in Figure 9 (e) and (f).

[A similar](#) degradation pattern of the impregnated Ni particles was therefore observed in all three cases, where small Ni particles aggregated to form large isolated Ni islands. However, the degradation of the CeO₂ phase [seems less considerable](#) to that of the Ni phase, as CeO₂ particles aggregated to form connected networks covering the ceramic backbone surface. The different degradation patterns observed above should therefore lead [to different](#) long-term degradation [rates](#) of the impregnated anodes.

3.6. Degradation mechanism

The long-term degradation mechanism of Ni-cermet anodes was also proposed by Klemenso *et al*, and they suggested that the dynamic reorganization of the Ni/NiO phase upon reduction and reoxidation accounts for the redox instability of the anode based on the DC conductivity measurements [17]. Here we [schematically](#) depict degradation mechanisms using different anode materials in Figure 10. Ni particles in the Ni-SSZ cermet suffered shrinkage and expansion during long-term redox cycling. Upon the oxidation of the anode, the well-percolating Ni phase cannot be fully oxidized into the original NiO-SSZ structure because of the Ni phase reorganization [during](#) reduction. Upon the reduction of the anode, the volume of the Ni phase reduced and adjacent connected Ni particles gradually sintered into each other forming rounded Ni particles. The microstructure of Ni phase changed [during](#) every redox cycle, which would be associated with the disconnection between the Ni phase and the SSZ phase (TPB loss) or even the fractures in the SSZ matrix. As a result, the Ni-SSZ can no longer provide an intact connected electronic conducting path, and thus anode-side ohmic loss increased after the redox cycling [16]. In addition, the break of TPBs reduced the electrochemical reaction sites inside the anode leading to the increase in anodic polarization and the cell performance deterioration [16, 17].

Much lower degradation [rates were](#) observed for the nano-catalyst impregnated anode, the main reasons of which may come from two aspects: Firstly, the robust electrical conducting paths provided by SLT-SSZ and SLT-GDC [are maintained](#) in redox cycling. It was demonstrated that the $\text{Sr}_{0.9}\text{La}_{0.1}\text{TiO}_3$ showed a relative expansion less than 0.05% in a wide range of oxygen partial pressure [19], and both GDC and SSZ show less than 0.5% relative expansion in the range of fuel cell operation [19, 20]. Microstructural [changes similar to](#) Ni-SSZ during the redox cycling cannot happen, and thus the anode-side ohmic loss intactly retained.

Moreover, as for the degradation of catalytic activity, aggregation and sintering of Ni particles indeed happened upon redox cycling, and therefore the electrochemical reaction sites were reduced. The aggregation phenomenon of impregnated Ni would be similar as that of Ni phase in the Ni-SSZ framework, but its negative effects were largely suppressed by structural advantages: The large isolated particles formed by aggregation still located on the conducting ceramic backbone, which avoided the [microstructural changes such](#) as in the conventional Ni-SSZ cermet, where the conducting Ni phase was redistributed and the Ni-SSZ connection (TPB) was destroyed and thus disconnected upon long-term redox cycles. The electrochemical reaction sites were therefore reduced.

The 50wt% partial substitution by nano-CeO₂ effectively suppressed the performance degradation. CeO₂ changed the volume less than 0.5% in the redox atmosphere [19], so the degradation could only happen in the initially loosely aggregated CeO₂ groups by long-term particle sintering. The positive effects by [the addition of](#) nano-CeO₂ in suppressing performance degradation may also come partially from its catalytic activity. It is widely accepted that CeO₂ is also a good catalyst for hydrogen oxidation even though not comparable with Ni [21]. The impregnated nano-CeO₂ provided additional electrochemical reaction sites for hydrogen oxidation, co-catalyzing the electrochemical reaction inside the anode. Suffering from the long-term redox cycling, the slightly degraded CeO₂ phase and the seriously degraded Ni phase could provide enough catalytic effect for the cells running in a low current density region because of the limited electrochemical reaction rate. In the high current density region, the slightly degraded CeO₂ phase and the seriously degraded Ni phase cannot provide [the](#) required catalytic effect for hydrogen oxidation [such](#) that voltage drop gradually increased as current density increased. [This is supported by](#) the I-V curve degradation in Figure 7 and the microstructural change in Figure 9.

It is therefore [desirable, in future, to](#) depress the microstructural changes of impregnated Ni and CeO₂ particles on the conductive oxide surface for further improvement in long-term durability.

4. Conclusions

The ceramic composite 60wt%GDC-40wt%SLT or 40wt%SSZ-60wt%SLT could be utilized as a robust anode backbone with excellent thermal stability and acceptable electrical conductivity. Excellent performance and improved redox stability could be achieved by impregnating nano-sized Ni particles as catalysts, compared with the conventional Ni-SSZ cermet anode. Moreover, partially substitution with CeO₂ maintained excellent performance and further improved redox stability of the Ni impregnated SLT cermet anode against redox cycling due to catalytic effects and minimized aggregation depressed by the presence of CeO₂ particles. As a consequence, the Ni and CeO₂ co-impregnated cermet with the SLT conductive backbone structure would be a promising robust SOFC anode.

Acknowledgments

This work was supported by Japan Science and Technology Agency (JST) through its “Center of Innovation Science and Technology based Radical Innovation and Entrepreneurship Program (COI Program)”. We thank Assistant Prof. Dr. George Harrington, Kyushu University, for carefully reading the manuscript.

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Captions

Figure 1. (a) SOFC single cell using different SLT composite functional layers, (b) schematic illustration of the nano-catalyst impregnated anode.

Figure 2. (a) Anode-side ohmic loss and (c) anodic overpotential of SOFC single cells using different SSZ-SLT composite; (b) anode-side ohmic loss and (d) anodic overpotential of SOFC single cells using different GDC-SLT composite.

Figure 3. (a) I-V curve and (b) anodic polarization of SOFC single cell using the S40 backbone, the 10wt% Ni impregnated S40 anode, and the 10wt% Ni-10wt% CeO₂ co-impregnated S40 anode.

Figure 4. (a) I-V curve and (b) anodic polarization of SOFC single cell using the G60 backbone, the 10wt% Ni impregnated G60 anode, and the 10wt% Ni-10wt% CeO₂ co-impregnated G60 anode.

Figure 5. Terminal voltage of single cells using (a) the 20wt% Ni impregnated G60 anode, (b) the 10wt% Ni-10wt% CeO₂ co-impregnated G60 anode, and (c) the 10wt% Ni-10wt% CeO₂ co-impregnated S40 anode during the first 10 redox cycles.

Figure 6. (a) Anode-side ohmic loss and (b) anodic polarization of three different anodes: the 20wt% Ni impregnated G60 anode, the 10wt% Ni-10wt% CeO₂ co-impregnated G60 anode, and the 10wt% Ni-10wt% CeO₂ co-impregnated S40 anode during the 50 redox cycles.

Figure 7. The I-V curve of SOFC single cells using different anode materials before and after the 50 redox cycles: (a) the 20wt% Ni impregnated G60 anode, (b) the 10wt% Ni-10wt% CeO₂ co-impregnated G60 anode, and (c) the 10wt% Ni-10wt% CeO₂ co-impregnated S40 anode.

Figure 8. Performance degradation of SOFC single cells using different anode materials at 200mAcm⁻² in the first 10 redox cycles and in the entire 50 redox cycles. The value for the Ni-SSZ anode was taken from Ref. 16.

Figure 9. The microstructure of the catalyst impregnated SLT composite anode before and after the redox cycling test: (a), (b) the 20wt% Ni impregnated G60 anode; (c), (d) the 10wt% Ni-10wt% CeO₂ co-impregnated G60 anode; and (e), (f) the 10wt% Ni-10wt% CeO₂ co-impregnated S40 anode.

Figure 10. Anode degradation mechanisms during redox cycling test with/without impregnation (Grey particles: oxide, green particles: Ni, white particles: CeO₂).

Figure 1. (a) SOFC single cell using different SLT composite functional layers, (b) schematic illustration of the nano-catalyst impregnated anode.

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462 Figure 2. (a) Anode-side ohmic loss and (c) anodic overpotential of SOFC single cells using
 463 different SSZ-SLT composite; (b) anode-side ohmic loss and (d) anodic overpotential of SOFC
 464 single cells using different GDC-SLT composite.

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Figure 3. (a) I-V curve and (b) anodic polarization of SOFC single cell using the S40 backbone, the 10wt% Ni impregnated S40 anode, and the 10wt% Ni-10wt% CeO₂ co-impregnated S40 anode.

Figure 4. (a) I-V curve and (b) anodic polarization of SOFC single cell using the G60 backbone, the 10wt% Ni impregnated G60 anode, and the 10wt% Ni-10wt% CeO₂ co-impregnated G60 anode.

Figure 5. Terminal voltage of single cells using (a) the 20wt% Ni impregnated G60 anode, (b) the 10wt% Ni-10wt% CeO₂ co-impregnated G60 anode, and (c) the 10wt% Ni-10wt% CeO₂ co-impregnated S40 anode during the first 10 redox cycles.

Figure 6. (a) Anode-side ohmic loss and (b) anodic polarization of three different anodes: the 20wt% Ni impregnated G60 anode, the 10wt% Ni-10wt% CeO₂ co-impregnated G60 anode, and the 10wt% Ni-10wt% CeO₂ co-impregnated S40 anode during the 50 redox cycles.

Figure 7. The I-V curve of SOFC single cells using different anode materials before and after the 50 redox cycles: (a) the 20wt% Ni impregnated G60 anode, (b) the 10wt% Ni-10wt% CeO₂ co-impregnated G60 anode, and (c) the 10wt% Ni-10wt% CeO₂ co-impregnated S40 anode.

Figure 8. Performance degradation of SOFC single cells using different anode materials at 200mAcm^{-2} in the first 10 redox cycles and in the entire 50 redox cycles. The value for the Ni-SSZ anode was taken from Ref. 16.

Figure 9. The microstructure of the catalyst impregnated SLT composite anode before and after the redox cycling test: (a), (b) the 20wt% Ni impregnated G60 anode; (c), (d) the 10wt% Ni-10wt% CeO₂ co-impregnated G60 anode; and (e), (f) the 10wt% Ni-10wt% CeO₂ co-impregnated S40 anode.

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Before redox cycles:

After redox cycles:

- Disconnection between Ni and SSZ.

➤ Electrical conducting path and TPB were deteriorated.

- Aggregative growth of Ni particles.

➤ Electrochemical reaction sites were deteriorated.

- Aggregated Ni particles and retained CeO_2 particles.

➤ Electrochemical reaction sites loss was suppressed.

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550 Figure 10. Anode degradation mechanisms during redox cycling test with/without impregnation

551 (Grey particles: oxide, green particles: Ni, white particles: CeO_2).

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