Anode supported SOFC fabricated with functional anode: role of variation of fuel and oxidants

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Abstract. The present study focuses on the efficacy of core-shell nickel (Ni) @ stabilized zirconia (SZ) functional anode towards the oxidation of both hydrogen and reformed methane as fuel in presences of steam as one of the important component. The redox reaction is processed by adsorption on anode catalyst followed by decomposition and charge transfer reaction. This is further accelerated by the extension of triple phase boundary (TPB) regions (Ni/SZ/gas) within (intra-) and inter-anode involving electrolyte. Core-shell Ni@SZ cermet enables the extension of TPB regions in contrast to conventional matrix. Authors have reported four configurations for anode support, wherein the layered structure involving conventional Ni-SZ is placed at the fuel side and layers of Ni@SZ on the top. The thin anode layer in vicinity to the electrolyte with optimized Ni content of 28/32 vol % acts as the primary electrocatalytic layer and shows a maximum current density of ~4 A.cm$^{-2}$@0.7 V, 800°C with moist hydrogen as fuel. Multifuel capability in the cell with similar functional anode is demonstrated using 20% reformed methane with optimum steam/carbon ratio (2:1) having current density of ~ 1.13 A.cm$^{-2}$ under similar condition. The findings are correlated using impedance spectroscopy and corroborated with morphological findings.

1. Introduction

In the present world, the primary important requisite is the demand of energy due to increasing industrialization and population. According to International Energy Agency (IEA) world energy outlook 2005, energy demand tends to increase by 50% by 2030. At the same time, the demand for green energy is accelerating in order to avoid rising green house gas emission, which results into deterioration of climate system. Fuel cell is an electrochemical device that is capable of converting the chemical energy of a fuel (hydrogen, CO, methane, hydrocarbons etc.) and an oxidant (air or oxygen) into electricity without combustion and bypassing the Carnot cycle. Owing to such fact, the theoretical efficiency of fuel cell is reported to be more than unity. Fuel cells are being classified on the basis of type of electrolyte and electrode materials. For all solid components, the operating temperature can be varied from 600–1000°C and termed as Solid oxide fuel cell (SOFC). SOFC is under development for
central station and dispersed power generation. The primary requisites of an electrolyte is to be dense, thin and either proton or oxide ion conductor for carrying out the electrochemical redox reactions [1].

Applicability of any specific composition in an anode-supported planar solid oxide fuel cell (SOFC) as an anode demands the fulfilment of certain properties eg. Thickness, electronic conductivity, sufficient interconnected porosity and electrocatalytic activity [2]. Optimization of anode morphology through appropriate processing techniques can play a significant role towards its activity in the single cell. Designing and controlling the anode microstructure is therefore important to satisfy the basic requirements of extending triple phase boundary (TPB) and appropriate gas diffusion paths [3]. Composite of Nickel (Ni)-yttria stabilized zirconia (YSZ) is a widely accepted anode which could be prepared by multiple techniques viz. conventional solid state mixing, sol gel processing etc [1]. The conventional Ni-YSZ anode synthesized through solid state mixing is reported to utilize ~ 40 vol% Ni for catalyst activity thereby results in thermal incompatibility problem with other cell components [4-5]. In addition, such anode is susceptible to long term degradation which can be ascribed due to the agglomeration of Ni particles at high operating temperature (800 -1000°C) [1]. Werber [6] reported that, insufficient removal of water vapour (formed during electrochemical reaction during high temperature operation of single cell) also results in Ni oxidation thereby causing agglomeration.

The aforementioned shortcomings of conventional anode could be resolved using functional Ni@SZ cermet with a core-shell morphology already reported in our earlier publications [7]. Such cermet requires only ~ 28 vol % of Ni to meet the electrical conductivity for SOFC operation [8]. The unique core-shell microstructure enables interconnecting network of Ni, YSZ and pores throughout the cermet matrix. The short and long term efficacy of such functional cermet with respect to hydrogen as a fuel and oxygen as oxidant is already reported in our early communications [9]. However, for up scalability and wider applicability, functionality of anode needs to be studied with respect to variable fuel and oxidant. The electrical efficiency of a fuel cell is strongly dependent on the kinetics of fuel oxidation and oxidant reduction mechanism [1]. Regarding the fuel oxidation, several theories predict significant contribution of either electrolyte or electrode components [1]. The study by Ong et al and Nguyen et al indicated that, electrolyte play a pivotal role in the oxidation of H2 and hydrocarbons [10, 11]. On a similar note, the presence of a small quantity of H2O in the fuel gas is proposed to influence the oxidation mechanism of both hydrogen and hydrocarbons. Studies have reported significant reduction in polarization losses and electrode resistance in moist fuel [12-14]. The present study intends to study the feasibility of such functional core-shell anode in variable fuel conditions. In such context, it is important to mention that, such Ni@SZ cermet posses’ sharp unimodal pore size distribution as reported by the author’s [15] which could effectively accelerate the electrochemical reactions at electrode/electrolyte interface. However, the initial feeding of the fuel towards the anode catalyst suffers significant hindrance owing to such symmetric mode of pore size distribution. Hence, a series of anode configurations have been proposed by the authors’ combining both conventional and core-shell anode in layered configuration. The novelty of the research work is to optimize the anode configuration effective for operating under mixed fuels like reformed methane containing mixtures of CO, H2 and steam. The single cells fabricated using such variable anode configurations are studied for their electrochemical performance evaluation and are correlated with morphological studies.

2. Experimental

SOFC anode powders were prepared by two techniques viz. a) conventional solid state route (NiO-YSZ) and b) particulate deposition route (Ni@SZ). The preparation of Ni@SZ anode is available in our earlier publications [16, 17]. For single cell fabrication, simple and up-scalable processing techniques viz. tape casting and screen printing were used [18, 19]. The details on type of anode supported structures categorized by Configuration I to IV are shown in Figure 1. It has already been established from electrical conductivity studies that, conventional anode matrix require ~ 40 vol % Ni to satisfy the electrical conduction required for SOFC application. However, such functional
Ni@SZ cermet require only ~ 28 vol % Ni to initiate the conductivity percolation [17]. Fabrication of half cells involved an initial tape casting of anode layers with variation in Ni content and porosity as well as that of a thin layer of YSZ electrolyte. This was followed by lamination of the anode layer(s) together with that of an YSZ layer at room temperature and co-sintering at around 1400°C to form the half cells with layered anode structure. During the lamination process, the conventional NiO-YSZ tapes (~ 40 vol % Ni) with higher porosity were used towards the fuel inlet for better gas diffusion and current collection. Ni@SZ anode tape(s) with much lower Ni content (~ 32 vol %) having lower porosity compared to the conventional cermet was placed onto the base support structure. Finally, the third layer(s) of electroless anode having still lower Ni content (~ 28 vol %) and porosity was placed adjacent to the YSZ electrolyte to have the half cell with a trilayered anode (TLA) structure. Similarly, half cells having bilayered anode (BLA) structure were fabricated consisting of conventional NiO-YSZ as the base support and Ni@SZ with 32 vol. % Ni. In Configuration I, II and III, the thickness of either Ni-YSZ or Ni@SZ was maintained at 50 µm. However, in Configuration IV (trilayer structure), a thin layer (~ 15 µm) of either 28/32 Ni@SZ tape was laminated onto the bilayer support consisting of thick Ni-YSZ and core-shell Ni@SZ monolith. After sintering of the half cell, thick pastes of lanthanum strontium manganite (LSM) and YSZ (1:1) were screen printed for cathode active layer (CAL) and LSM for cathode layers (CL) respectively onto them. Single cell (~ 16mm) was obtained upon co-sintering of the screen printed cathodes at around 1100°C [16-19].

![Figure 1. Schematic for anode configurations fabricated using conventional and core-shell anode](image)

Electrochemical property evaluations of single cells were performed using variable fuels like hydrogen (with 3% moisture) and 20 % reformed methane (40 % RH) with oxygen and air as the oxidant in the temperature range of 700-800°C. The observed electrochemical activity of the aforesaid cells were correlated with the corresponding microstructures obtained using high resolution microscope (Olympus GX 71, Japan) and field emission scanning electron microscope [FESEM] (Gemini Supra 35, Zeiss) respectively.
3. Results and Discussion

3.1. Role of moisture in the SOFC performance with $H_2$ as the fuel

The electrochemical behaviour of hydrogen oxidation is significantly influenced by the presence of water or oxygen containing molecules in the fuel. The kinetics of hydrogen oxidation is known to be related with the oxygen activity on Ni surface [1]. Moisture from the fuel undergoes dissociative decomposition to produce oxygen species which readily get adsorbed on the Ni surface.

$$H_2O \rightarrow O_{ad,Ni} + H_2$$  \hspace{1cm} (1)

According to the mechanism, both YSZ and Ni contribute towards dissociative $H_2$ adsorption (Eq. 2) at anode. This is followed by charge transfer reaction of adsorbed $O^{2-}$ ion from YSZ to Ni species at active anode (Eq. 3) and thereby water is formed as the final by product by releasing electrons to the external circuit.

$$H_2 \rightarrow H_{ad,YSZ} + H_{ad,Ni-O} (on \ O_{ad,Ni} \ in \ Eq.5.51)$$  \hspace{1cm} (2)

$$O^{2-}_{ad,YSZ} + O_{ad,Ni} \rightarrow O_{ad,YSZ} + O^{2-}_{ad,Ni} \Rightarrow O^{2-}_{ad,Ni} \rightarrow O_{ad,Ni} + e^-$$  \hspace{1cm} (3)

$$2H_{ad,YSZ} / 2H_{ad,Ni-O} + O_{ad,YSZ} / O_{ad,Ni} \rightarrow H_2O \ (Anode \ product)$$  \hspace{1cm} (4)

The decomposition of moisture therefore initiates the reaction path through bulk anode and propagates it towards the electro-active zone at the anode/electrolyte interface. This active zone contributes in the charge transfer reaction and finally forms product at the anode outlet. The content of moisture in the fuel has already been optimized to $\sim 3 \%$, exceeding of which tends to enhance the interfacial resistance thereby reducing the overall cell performance [20]. An experimental outcome is presented in this section regarding the role of reactant gasses towards the cell performance. Four different experiments are carried out based on the variation of composition of reactant gasses to study the cell performances with varied anode configurations as shown in Figure 1. The detailed study on I-V characteristics of single cells fabricated using five configurations as a function of gas flow rate is shown in Figure 2. The details on variation of gas compositions carried out in four separate experiments (Experiment 1 to 4) are also given in Figure 2. It is observed from the figure that, irrespective of anode configuration, similar trend is observed in cell performance for all four experiments (I to IV). From experiment-I, it can be observed that systematic increase in the flow rate of fuel from 20 to 200 SCCM linearly enhance the electrochemical performance of the cell. However, increasing the fuel flow rate beyond 200 SCCM does not contribute towards further enhancement of cell performance, owing to which the optimum flow is fixed at 200 SCCM. At lower fuel content, the saturated moisture uptake of fuel also happens to be less, due to which the number of oxygen species required for effective adsorption of entire catalytic Ni-sites is insufficient. As the flow rate is enhanced, the availability of such adsorbates ($O^{2-}$) is increased which accelerates charge transfer reaction in Eq. 3 towards the forward direction. However, upon increasing the fuel flow rate beyond saturation (highest current density in respective configurations) would simply provide excess $O^{2-}$ species without significant performance enhancement. The extent of performance increment is however observed to be marginal upon using dry $H_2$ as the fuel (experiment II) in which the initiation reaction (Eq. 1, 2) is absent.
Therefore, dry hydrogen tends to lower the overall cell performance due to the enhancement in associated interfacial resistance [20]. In contrast, variation in $O_2$ flow rate is found to have negligible contribution to the overall performance of single cell as observed in either of the experiments III and IV. Therefore, moisture content in the fuel is found to impart significant role towards the oxidation of $H_2$ and electrochemical activity of the single cell. The tentative mechanism for Ni@SZ catalyzed $H_2$ oxidation reaction is shown in Figure 3. The process involves primarily an initial gas adsorption onto catalyst surface followed by necessary dissociation and diffusion to form steam as the product.

**Figure 2.** Plot of current density vs. Gas flow rate for fuel fabricated with anodes of: a) Configuration I, b) Configuration II, c) Configuration III-BLA, d) Configuration IV-TLA1 and e) Configuration IV-TLA2 ** details of EXPERIMENT is given in the figure.
However, the electro catalyst reaction initiates with the decomposition of any oxygen containing species (eg. H$_2$O) which can act as active adsorbed species on Ni surface and propagates the hydrogen oxidation reaction. The subsequent charge transfer reaction also involve such active oxygen sites which in turn correlates both Ni and SZ species for producing steam as product with least activation and diffusion over potentials. Such intricate fuel hydrogen oxidation process requires active participation of both Ni and SZ species and hence accelerated in presence of triple phase regions (Ni, SZ and gas phase). Core-shell anode enables the generation of dual triple phase boundary (TPB) regions in the anode interior (intra-TPB) and anode/electrolyte junction (inter TPB) in comparison to conventional cermet. Such TPB regions within the conventional cermet are not continuous but discrete and limited. Functionality of such core –shell anode is envisaged from higher cell performance of Configuration III in comparison to either Configuration I or II. As already stated above, bilayer configuration is more effective compared to either of the pristine system owing to the fact that, the support anode allows easy diffusion of hydrogen fuel and the electrochemically active core-shell anode with unified pore size distribution performs efficient catalytic oxidation of fuel. Furthermore, trilayer structure is proposed by the authors’ in Configuration IV wherein a thin layer (15 µm) of 28 vol % Ni (Configuration IV-TLA1) and 32 vol % Ni (Configuration IV-TLA2) is casted onto the bilayered anode monolith consisting of conventional Ni-SZ and core-shell Ni@SZ of 32 vol % Ni. Such configuration is observed to show maximum cell performance of ~ 3.7 A.cm$^{-2}$ at 0.7 V@800°C. Further increase in performance (4.1 A.cm$^{-2}$) is noted with increase in Ni content to 32 vol % in the thin anode active layer in Configuration IV-TLA2. However, with increase in Ni content in the electro catalyst layer to 40 vol % at the vicinity of electrolyte, the performance is observed to get reduced.

**Figure 3.** Schematic for mechanism of fuel oxidation at anode/ electrolyte interface
This can be explained on the fact that, upon increasing the Ni content beyond the optimized limit as reported by Mukhopadhyay et al [8], the outer shell becomes thick thereby limiting the contribution from core SZ matrix. This limits the triple phase boundary regions which accelerate the associated activation and diffusion polarization, owing to which the cell performance is reduced (not given here).

3.2. Dependence of cell performance on type of oxidant

It has been observed during the course of experiments that, in spite of employing optimized anode configuration in selected fuel environment at anode compartment, cell performance tends to reduce drastically with variation of oxidant. SOFC being an example of open system, it is primarily governed by the concentration of reactant gasses (fuel and oxidant) expressed in the form of partial pressure terms as:

\[ V(I) = V^o + \frac{RT}{4F} \ln(p_O^o) + \frac{RT}{2F} \ln\left(p_{H_2}^o\right) - \frac{RT}{2F} \ln\left(p_{H_2O}^o\right) \]  

where, \( V(I) \), \( V^o \), \( p^o \), \( R \) and \( T \) are experimental voltage under load, standard Nernst potential, partial pressures of concerned gasses outside anode or cathode compartment, universal gas constant and operating temperature of the cell respectively. Therefore, it could be said from Eq. 5, that the electrochemical reaction is linearly proportional to the partial pressure of oxygen \( [V(I) \propto p^o_O] \) gas used as oxidant at the cathode side.

The electrochemical performances of single cells fabricated with all experimental anode configurations in the oxidant environment of both ‘oxygen and air’ are compared in Figure 4.

![Figure 4](image)

**Figure 4.** Comparative performance evaluation of single cell in two oxidants viz. oxygen and air

It can be observed that, irrespective of anode configurations, significant deterioration in cell performance is obtained with air as oxidant. Such observation is based on the factors effecting oxidant reduction reaction at cathode and the associated polarization generated through the reactions.
The overall reaction for the oxygen reduction reaction (ORR) at SOFC cathode is given as [1]:

\[ O_2 + 2V_o^+ + 4e^- \rightarrow 2O_o^+ \]  

The reaction given in Eq. 6 is made up of a series of bulk and surface processes. The mechanistic contribution to cathode polarization losses \( R_{\text{Cathode}} \) can be written as [21]:

\[ R_{\text{Cathode}} = R_{\text{Gas diffusion}} + R_{\text{Surface adsorption diffusion}} + R_{\text{Charge transfer}} + R_{\text{ohmic}} \]  

where, ‘R’ terms refers to the various polarization factors offered towards overall cathode polarization. Eq. 7 can be modified as [1]:

\[ V(I) - V^o = \frac{RT}{4F} \ln(p_{O_2}^o) + \frac{RT}{2F} \ln(p_{H_2}^o) - \frac{RT}{2F} \ln(p_{H_2O}^o) \]

\[ = R_{\text{Cathode}} + R_{\text{Anode}} + R_{\text{Electrolyte}} + R_{\text{Other factors}} = \eta \]

\[ = R_{\text{Cathode}} + R_k \]

where, \( \eta \) is the overall cell polarization and \( R_k \) is the resultant polarization contributed from all other terms except cathode.

Therefore, upon combing Eqs. 7 and 8, we can have:

\[ R_{\text{Cathode}} = \left[ \frac{RT}{4F} \ln(p_{O_2}^o) + \frac{RT}{2F} \ln(p_{H_2}^o) - \frac{RT}{2F} \ln(p_{H_2O}^o) \right] - R_k \]

\[ \Rightarrow R_{\text{Cathode}} \propto p_{O_2}^o \]

Eq. 9 clearly describes the linear correlation of cathode polarization with partial pressure of oxygen. Therefore, reduction in electrochemical performance of the single cells with air is mainly because of reduced oxygen reaction rate (ORR) at the cathode compartment due to the reduced partial pressure of oxygen [22]. Enhanced anodic electrochemical activity for the single cells having Configuration-IV-TLA2-series anode though accelerates the overall performance, but higher cathodic polarization generated upon using air as the oxidant contributes significantly towards diminishing the activity of the single cell.

3.3. Influence of reformed methane on the cell performance of FC with Configuration IV

The study reported in section 3.1 and 3.2 establish that among the four selected anode configurations, Configuration IV-TLA 2 is proved to be the optimized one. Maximum current density of \( \sim 4.1 \) A.cm\(^{-2}\) is obtained at 0.7 V @800°C for coupon FC’s fabricated using anode of such configuration. Based on such observation, applicability of such anodes is proposed to get tested in other fuels like 20 % reformed methane which comprises of a mixture of H\(_2\) and CO. Literature study reports that, such Ni/SZ based composites act as suitable catalyst for steam reformation of methane [23]. The mechanism for oxidation of reformed methane as fuel is given in Figure 3. The redox reaction comprise of SMR (steam methane reformation) and water gas shift reaction (WGS) as shown in the figure and Eq. 10, 11 respectively.

\[ CH_4 + H_2O \rightarrow CO + 3H_2 \]  

\[ CO + H_2O \rightarrow CO_2 + H_2 \]  

The first reaction is reported to be strongly endothermic (\( \Delta H = 206 \) kJ.mol\(^{-1}\)) whereas the second reaction is found to be slightly exothermic (\( \Delta H = -41 \) kJ.mol\(^{-1}\)). The primary limitation of using Ni based catalyst in such SMR reaction is the Oswald ripening phenomena wherein the metal phase tend to ripe and form island thereby reducing the net catalyst surface area and functionality [23]. Nakagawa
et al has reported the catalytic activity of Ni-YSZ-CeO$_2$ for steam reforming of methane in a direct IR (internal reforming)-SOFC [24]. The ceria phase is proposed to protect the anode (i.e catalyst) from blocking by carbon deposition when the steam to methane ratio in the reaction gas (S/C) is smaller than a critical value. However, compared to Ni-YSZ, catalyst activity of Ni-YSZ-CeO$_2$ is found to be superior only at low temperature. At high temperature with low partial pressure of hydrogen ($P_{H_2}$) and high $P_{H_2O}$, catalytic activity suffers gradual deterioration due to non functionality of CeO$_2$ (at high temperature) and oxidation of Ni to NiO as well as ripening of Ni (since > 50 vol% Ni is present) [24]. In line of such observations, the author’s studied the efficacy of functional core-shell Ni@SZ based anode for such reformed methane as fuel. Performance evaluation of FC fabricated with Configuration IV-TLA 2 anode is only reported in Figure 5a. The steam to carbon ratio is varied from 0.5 to 2.5 as shown in the figure. As already stated in section 3.1 that, presence of oxygen containing species like H$_2$O in fuel accelerates the reaction rate with least polarization losses. The mechanistic approach is illustrated in Figure 3 which shows the reaction initially process through surface adsorption and dissociation onto Ni/SZ surface to form CO and H$_2$ as the intermediate by product. The produced hydrogen and carbon monoxide can be readily oxidised electrochemically at the triple phase boundary (TPB/ Ni-SZ-gas) thereby catalysing the completion of the reaction to form CO$_2$ and H$_2$O. Furthermore, it could also be stated that, the SZ phase bears significant contribution towards catalyst activity through oxide ion conduction thereby catalysing the final product formation of CO$_2$ and H$_2$O. Owing the presence of core-shell morphology at optimized Ni content of 32 vol % in Ni@SZ cermet, contribution of both SZ and Ni phases is functional compared to the dispersed morphology of Ni-SZ.

The addition of steam to hydrocarbon fuel is necessary for both reformation and water gas shift reaction that initiates at anode. In addition, steam is added in excess of its stoichiometry to reduce the risk of carbon deposition (Eq.12).

$$2CO \rightarrow CO_2 + C \downarrow$$

$$CH_4 \rightarrow C \downarrow + 2H_2$$

In line of such discussion, it is obvious that, with an initial increment in steam to methane ratio (S/C), the cell performance steadily increases from 0.67 A.cm$^{-2}$ to 1.13 A.cm$^{-2}$ till S/C = 2.0 (shown in Figure 5a). The associated cell ASR values are also observed to follow a reducing trend (Figure 5b) upon
steady increase in the steam content within the fuel. However, further enhancement in the S/C ratio to 2.5 is found to reduce the cell performance magnitude to 0.96 A cm$^{-2}$ with increased ASR of $\sim 452 \Omega \cdot \text{cm}^2$. This could be explained on the fact that, with subsequent increase in the steam is desirable for the mitigation of coke, however, it act as a diluent thereby reducing the cell voltage and lead to rapid degradation of anode. In addition, excess steam tend to degrade the anode by oxidising the metallic component thereby result in significant volume expansion and limits the extension of TPB regions from intra-anode to inter anode regions. Study on the fuel cell performance evaluation using reformed methane with variable steam: carbon ratio is carried out using air as the oxidant. The significant point to highlight is the higher cell performance of FC fabricated with anode of Configuration IV-TLA2 using moist hydrogen as fuel ($\sim 4.1 \text{ A.cm}^2$) compared to maximum performance of $\sim 1.13 \text{ A.cm}^2$ at S/C: 2 under similar experimental conditions. This suggests slower electrochemical oxidation step for methane which generally arises due to significant activation barrier. Aslannejad et al [25] further stated that reduced power density for methane with respect to hydrogen may be correlated with the higher mass of methane molecules. This variation in size generates slower gas phase diffusion and enhanced concentration polarization.

Similar observation to congruent to the cell performance is observed from the cell impedance study is reported in Figure 6.

Figure 6. Impedence spectra of single cell fabricated with anode of Configuration IV-TLA2

Nyquist plot for FC fabricated with anode of Configuration IV-TLA2 at S/C = 2 is only reported in this figure within operating temperature range of 700°C to 800°C. With increasing operating temperature from 700-800°C, the arcs are found to be depressed showing lower cell polarization resistances. This could be defined based on the enhanced electrochemical reaction with increase in operating temperature which reduces the energy barrier for the rate determining steps represented by each arc. The low frequency arc is primarily responsible for the diffusion of fuel and oxidants and the deconvolution of the two arcs are found to be merged at the higher temperature of operation of 800 °C. The $R_p^2$ for the gas diffusion is found to be 2.76 $\Omega \cdot \text{cm}^2$ at 700 °C and that has been reduced down to 1. 16 $\Omega \cdot \text{cm}^2$ at 800 °C. $R_p$ is representable for the cell polarization and is found to be minimum 0.2 m$\Omega \cdot \text{cm}^2$ at 800 °C. The total ohmic resistance of the single cell fabricated with such functional anode
is found to be $1.45 \, \Omega \cdot \text{cm}^2$ at 800 °C. Anode of configuration IV TLA-2 also helps in lowering the resistance of electronic flow path by minimizing the intra anodic stratum. Consequently the cell with 32 AAL-2 exhibits least polarizations as observed from the impedance spectra. Therefore, incorporation of electroless in conjugation with conventional anode tends to significantly enhance the electrochemical performance of single cell with reduced polarization losses.

![Image](image.png)

**Figure 7.** a) SEM image of single cell fabricated with layered anode, b) EDAX imaging of Zirconia mapping of the single cell. SEM microstructure of: c) core-shell Ni@SZ and d) conventional Ni-SZ.

The observations are further supported by the morphological study shown in Figure 7. The functionality of core-shell anode is shown in Figure 7b wherein the nano Ni in the form of discreet shell is surrounded onto core SZ. The interconnection among both the phases is maintained throughout the matrix by such functional synthesis technique. However, distribution of dispersed Ni and SZ phases are observed in the matrix of conventional Ni-SZ anode. The microstructure of single shell shows trilayer anode configuration with catalytic Ni@SZ in vicinity of electrolyte and conventional anode towards support structure to allow easy fuel diffusion.

4. Conclusions

In a nutshell, it could be stated that, in the present investigation, the author intend to fabricate solid oxide single cell (s) using in house developed functional Ni@SZ anode. The prime novelty of such functional anode is the formation of unique core-shell structure wherein nano Ni is discreetly distributed onto core SZ. Such morphology enables interconnection among both Ni and SZ phases throughout the anode matrix thereby generating triple phase boundary (TPB) regions [Ni/SZ / gas during operational SOFC] within (intra-anode) and inter (anode/SZ electrolyte) regions. Author’s have
proposed four configurations I-IV. In the initial two configurations, conventional and core-shell composite form the anode support. From Configuration III onwards, layered structure of anode is fabricated. In such bi-or trilayered matrix, conventional anode acts as the primary gas diffusion layer. The Ni@SZ anode is placed onto the support conventional matrix adjacent to the ion conducting SZ electrolyte. This functional layer act as an effective catalyst for electrochemical reaction at the anode/electrolyte interface by initializing the reaction through adsorption, dissociation and decomposition of fuel gas molecules. Through this mechanism, author’s have proved the requirement of oxygen containing species to be present along with fuel gasses for maximization of fuel cell performance. Single cells with trilayered anode configuration are found to exhibit maximum cell performance of 4.1 A.cm\(^{-2}\)@ 0.7 V and 800°C. In contrast, due to slower activation kinetics, fuel cell fabricated with similar anode shows much less performance of only 1.13 A.cm\(^{-2}\)@ 0.7 V and 800°C with reformed methane as the fuel. However, compared to the performance of single cell fabricated with anode of Configuration I (0.67 A.cm\(^{-2}\)), anodes of Configuration IV-Trilayer (TLA) 2 is much more functional with methane as the fuel and at an optimized steam/ carbon ratio of 2. Upon increasing the steam/methane ratio beyond 2, the cell performance drops down to 0.96 A.cm\(^{-2}\)@ 0.7 V and 800°C. The total ohmic resistance (of the single cell fabricated with such functional anode is found to be 1.45 \(\Omega\).cm\(^{2}\) at 800 °C which increases to 3.15 \(\Omega\).cm\(^{2}\) at 700 °C. The \(R_p\) for the gas diffusion is found to be 2.76 \(\Omega\).cm\(^{2}\) at 700 °C and that has been reduced down to 1.16 \(\Omega\).cm\(^{2}\) at 800 °C. \(R_p\) is representable for the cell polarization and is found to be minimum 0.2 m\(\Omega\).cm\(^{2}\) at 800 °C. This could be explained on the fact that, with subsequent increase in the steam is desirable for the mitigation of coke, however, it act as a diluent thereby reducing the cell voltage and lead to rapid degradation of anode. In addition, excess steam tend to degrade the anode by oxidizing the metallic component thereby result in significant volume expansion and limits the extension of TPB regions from intra-anode to inter anode regions. These observations are also supported from impedance and SEM morphological study. The cross section of single cells shows the layered microstructure of anode. The Ni mapping image clearly shows distinct three layers within anode matrix. The section of anode placed in vicinity of the electrolyte comprises of core-shell structure and is further divided into one thick casted layer followed by thin casted layer adjacent to the SZ electrolyte. Hence, it could be concluded that, such functional anodes possess excellent functionality towards electrochemical oxidation of multiple fuel. The associated coating reported with methane as fuel are also reduced significantly using such novel anodes. Future research is imbibed in the up scalability of such layered anode fabrication and performance evaluation of such fuel cells on both short and long term testing.

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