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Coking-Resistant Anodes for Solid Oxide Fuel Cells Fueled by Low-Concentration Coalbed Methane

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Abstract. Low-concentration coalbed methane has a low methane fraction and is highly diluted with N_2. This results in less fuel being available at the SOFC anode and carbon control is then an important issue in methane conversion. This review addresses three questions related to each other. How can the use of a fuel be constrained by low CH_4 content and N_2 dilution? Second, what is the reason for carbon's formation on Ni-based anodes? Third, how can ceria-based materials, reforming layers, steam, and CO_2 alter this behavior? Ni–YSZ is still used as the reference anode for its electronic conduction and methane activation. The same Ni surface can also catalyze the cracking of methane. The ceria-based phases can provide mobile oxygen near Ni and can help with the removal of carbon; the impact depends on the local interface. A reforming layer is used to convert some of the methane prior to reaching the main electrochemical region. Either steam or CO_2 can participate in the reforming or carbon gasification process; however, too much added results in lower methane content. None of these options completely overcome the restrictions imposed by a dilute methane feed. Therefore, their effectiveness depends on the primary anode limitation and the actual fuel composition.

Keywords: low-concentration coalbed methane, solid oxide fuel cell, Ni-based anode, coking resistance, catalytic reforming

1. Introduction

Large amounts of low-concentration methane-containing gas are generated during coalbed methane development and coal mine gas drainage. Although this gas has potential value as an energy resource, its CH_4 content is usually low and it often contains N_2, O_2, CO_2, and water vapor. As a result, the gas has a low calorific value. Direct combustion can then be difficult to ignite, hard to keep stable, and inefficient in energy use [1]. Solid oxide fuel cells (SOFCs) provide an alternative route for the utilization of such low-grade methane resources because they can convert the chemical energy of methane into electricity at high operating temperatures. Previous studies have shown that low-concentration coalbed methane can be used for power generation in SOFCs with the assistance of catalyst layers or modified anodes [2-4].

Ni-based anodes are common in SOFCs because Ni conducts electrons and activates methane. The anode also supports the electrochemical oxidation of H_2 and CO. These functions are useful, but

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the same Ni surface can promote carbon formation during methane conversion. Methane cracking and CO disproportionation are two main routes [5, 6]. Deposited carbon first covers exposed Ni sites. As it grows, it can narrow pores and restrict fuel transport. Reaction resistance then rises, and cell performance can fall during long operation.

In the case of low-concentration coalbed methane, the anode needs to be designed to compromise between methane conversion and carbon control. Here, three ways are considered. Oxygen-active oxides can be added near Ni, a reforming layer can be used to reform some of the methane prior to the main anode, and the composition of fuel can be modified to aid in removal of carbon. The focus of the review is thus on Ni-based anodes, carbon-forming reactions and practical coking control methods. The comparison is done on the basis of low-concentration methane, in terms of the impact of the methods on methane conversion, carbon removal and gas transport.

2. Challenges of low-concentration methane fuel

The low methane content restricts the amount of fuel getting to the anode. The CH_4 fraction of low-concentration coalbed methane (LC-CBM) is much lower than that in methane-rich feeds. The more the total gas flow is reduced, the less methane enters the cell. This results in less CH_4 to reform and available for subsequent electrochemical use. If conversion is incomplete, the amounts of H_2 and CO formed from methane also decrease. This is not just a problem of the catalyst, but also one of fuel supply. An anode which has been tested with concentrated methane may not respond in the same manner when fed with a diluted methane. Experimental research of LC-CBM SOFCs indicates that fuel utilization is influenced by the methane concentration [1, 3].

Nitrogen dilution adds another limitation. In many LC-CBM streams, N_2 makes up a large part of the inlet gas. It does not provide fuel for the anode and mainly lowers the methane fraction in the stream. Under similar total pressure and flow conditions, a larger N_2 fraction means less CH_4 is supplied to the anode. The gas therefore contains less usable fuel per unit volume. The anode must still convert the smaller amount of CH_4 that is present. For this reason, gas transport and catalytic conversion become more important as dilution increases [1, 3]. The effect of N_2 in this discussion is mainly dilution. It reduces the amount of methane available in the reaction region and makes low-concentration fuel more difficult to use than methane-rich feeds.

Carbon deposition is another type of problem. The surface of Ni can be active for methane conversion but it can also promote solid carbon formation. CH_4 can lose H in a series of steps on Ni. If the carbon species that remain are not removed quickly enough, the carbon remains on the surface. CO disproportionation, also called the Boudouard reaction, is another possible route to carbon formation [5, 6]. The initial carbon deposit covers part of the exposed Ni surface. As deposition continues, carbon begins to fill the pore space and hinder gas flow. The area of the electrochemically active surface is reduced and the amount of methane entering the reaction area is also decreased. These changes result in a loss of transport and decreased conversion. However, these losses are more significant under LC-CBM operation because the methane supply is limited. When active area is lost a greater proportion of the available fuel is thrown away. Carbon growth should therefore be limited during the conversion of the diluted methane for stable operation.

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3. Ni-based anodes in SOFCs

3.1. Advantages of Ni-based anodes

Ni–yttria-stabilized zirconia (Ni–YSZ) is a reference anode material for the conventional SOFCs. The two phases have different roles. The Ni is the predominant electron-conducting pathway and the catalytic sites. YSZ provides the electrode with a ceramic support, and transports oxide ions close to the reaction zone. During reduction, a porous electrode forms and fuel will be able to flow through the pores and get to Ni in the anode. The pore network creates extensive gas–Ni–YSZ triple-phase boundaries, which provide interfacial sites for electrochemical reactions. Ni–YSZ also can be used with existing SOFC processing techniques. Electronic and ionic paths are close to the gas-filled pores, which helps to linking the fuel conversion with the electrochemical reaction [5, 6]. These characteristics are also beneficial when future modifications to the surface or catalyst-layer are made. As such, Ni–YSZ is used as a reference to measure the performance of an added catalyst layer.

Methane must undergo an initial activation step prior to electrochemical oxidation, compared to the other fuels (H_2 or CO). Ni is capable of splitting C–H bonds, and can also catalyze reforming reactions to produce H_2 and CO. The products are then oxidized on the anode. In this way Ni–YSZ does not only help in fuel conversion but also in charge transfer. This dual function is important when the methane concentration is low. Only a small quantity of CH_4 enters the cell, and slow conversion can result in the partial use of that fuel before it leaves the anode region.

Ni–YSZ is also a long used material to fabricate SOFCs. Its reduction behavior and porosities are well established and its contact with YSZ electrolytes is known in SOFC cell design. This allows a common base anode in the case of low-concentration methane study. The additional functions can then only be added as and when required. For instance, a catalyst layer can be used for part of the reforming step, while an oxide phase can be used to aid in carbon removal [6-8].

3.2. Main problem: carbon deposition

A primary drawback of Ni for direct use of methane is carbon deposition. There are a number of surface steps involved in the dehydrogenation of methane on Ni. Some carbon is attached to the metal and it builds up, if the conversion of the carbon-containing intermediates is slow. CO can also be used to produce carbon. These routes can be represented by equations (1) and (2):

$$CH_4 \rightarrow C + 2H_2 \tag{1}$$

$$2CO \rightarrow C + CO_2 \tag{2}$$

A final carbon measurement does not show how the deposit developed during the test. Figure 1 illustrates this progression. Carbon first appears at local sites and then spreads over a larger part of the anode surface. As coverage increases, less Ni remains exposed. A thicker deposit can also obstruct the route by which fuel reaches the reaction zone. The figure therefore links carbon growth with both loss of surface activity and poorer gas access [6].

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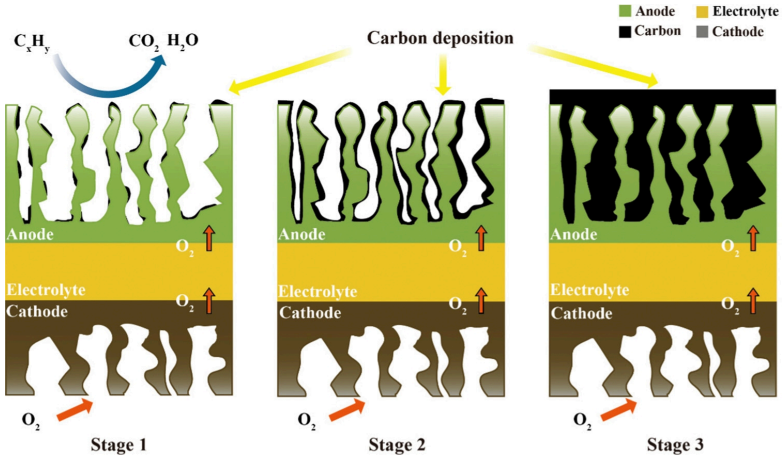


Figure 1. Schematic of the carbon deposition processes [6]

There are 2 effects which are most relevant to operation of the cell. The first is that Ni surface is lost: carbon blocks the accessible Ni surface which is necessary for methane activation and reforming. The other is a variation of pore space. There should be an open network for the movement of fuel through the anode in Ni–YSZ. Carbon in that network constricts passages, and can cause unequal local fuel supply. The more difficult it is for gas to flow, the more concentration is lost and some reaction areas are not adequately fueled. Carbon can also have the effect of decreasing the contact of the gas with the electrochemically active sites [5, 6, 9].

The consequences build up with time. Reducing the number of active Ni sites decreases methane conversion and a narrowing of pores increases the non-uniformity of the local gas composition. Both have a negative impact on performance. These effects are accentuated by the small amount of methane gas supplied at the inlet in LC-CBM operation. Less fuel is available to compensate for the loss of reaction area and gas access. Thus, coking does not only have an influence on surface chemistry, but also on mass transport and long-term anode behavior. The strategies below tackle various aspects of this issue. Some promote carbon removal, some convert methane before it reaches the main Ni region, and others modify the gas composition to reduce carbon adhesion to the anode.

4. Strategies for reducing carbon deposition

In this section three approaches are considered. They add ceria-based materials as close to Ni in order to help remove carbon species. A reforming layer converts the part of the methane before it reaches the Ni–YSZ anode. The inlet chemistry changes with steam or CO_2, which can react with and consume carbon. These solutions operate on various areas, and as a result, the limitations are different.

4.1. Adding ceria-based materials

Ceria-based materials, such as CeO_2 and gadolinia-doped ceria (GDC), may be combined with a Ni anode or in an adjacent catalytic layer. Ni remains the principal site for activation of methane. The ceria phase's contributions are primarily due to oxygen transport. The oxide can exchange oxygen with the gas and with other surface species in the vicinity of the oxide, through oxygen vacancies. Thereafter, the carbon-containing intermediates in the vicinity of Ni can be oxidized to gaseous products rather than forming solid deposits [6, 8].

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This method is most beneficial when carbon is being formed at a rate which is faster than the rate at which the anode is removing carbon. Just raising the activity of Ni may exacerbate that imbalance, since raising the activity of the Ni could lead to greater amount of carbon-containing intermediates. Another pathway for their oxidation is provided by ceria near Ni, which can also participate in reactions with CO_2 or H_2O. The core-shell system in [8] is one of them. It successfully sustained the conversion of methane in a long test using low-concentration methane. What is significant here is not a single power density value but the stability of the catalytic region over time.

Ceria-based modification does not stop methane from reaching Ni. Methane cracking can still occur. The effect also depends on how well the ceria phase contacts Ni and whether oxygen species can move to the places where carbon forms. If the interface is poor, the added oxide may contribute little to carbon removal. This approach is therefore better suited to an anode in which carbon oxidation is the main limitation.

4.2. Using a catalytic reforming layer

A reforming layer changes where methane is first converted. The layer is placed on or before the main Ni-based anode. Part of the incoming methane is converted to H_2 and CO in this region. The main Ni–YSZ anode then receives a fuel that contains more reforming products and less unconverted methane. This reduces the amount of direct methane dissociation required on the electrochemical anode. It can also separate the strong reforming reaction from the main electrochemical reaction zone.

Reference [7] reports an additional Ni–Fe reforming layer for low-concentration coal mine gas. As shown in Figure 2, the cross-sectional scanning electron microscopy (SEM) images reveal a distinct porous Ni–Fe region above the conventional anode. The interface appears continuous, and the added layer contains open pore space. This structure gives the inlet gas a separate catalytic region before it reaches the main anode. The image therefore supports the proposed placement and transport function of the reforming layer [7].

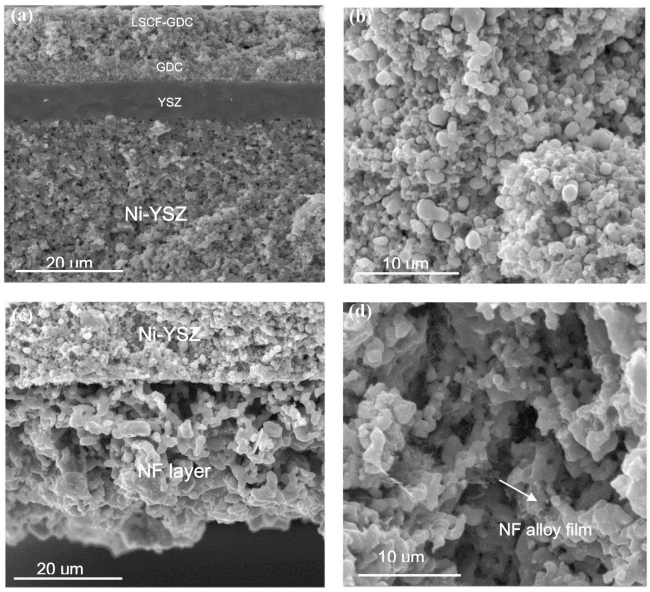


Figure 2. Cross-sectional SEM images of cell #1 with an NF (Ni–Fe) reforming layer [7]

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Long-term operation in the same study provides the more direct evidence for carbon resistance. The cells were tested with strongly diluted methane mixtures, including fuels containing N_2, H_2O, and O_2. Stable operation was maintained for more than 100 h. Post-test examination did not show obvious carbon accumulation on the main anode or the Ni–Fe layer [7]. The long-term test and post-test characterization support the conclusion on coking resistance. Taken together, the results suggest that moving part of methane conversion to a separate Ni–Fe region can reduce the carbon load on the main Ni–YSZ anode.

This method also has a limitation. The added layer becomes another gas transport region. Its pore structure and thickness must allow fuel to pass through without creating a large diffusion loss. Good contact with the main anode is also necessary. A dense layer can slow gas movement, whereas a weak interface can become unstable during extended operation. The reforming layer is therefore helpful when direct methane conversion on Ni is a major source of carbon, but it should not create a new transport bottleneck.

4.3. Adjusting the fuel with steam or CO_2

The reactions at the anode change with the introduction of steam and CO_2, but the basic electrode material does not. Steam can be involved in the methane reforming and can react with deposited carbon. CO_2 may participate in dry reforming and carbon gasification. In both processes, solid carbon can be transformed to gas phase products. H_2 or CO can also be formed by the same reactions and can be electrochemically utilized [10, 11].

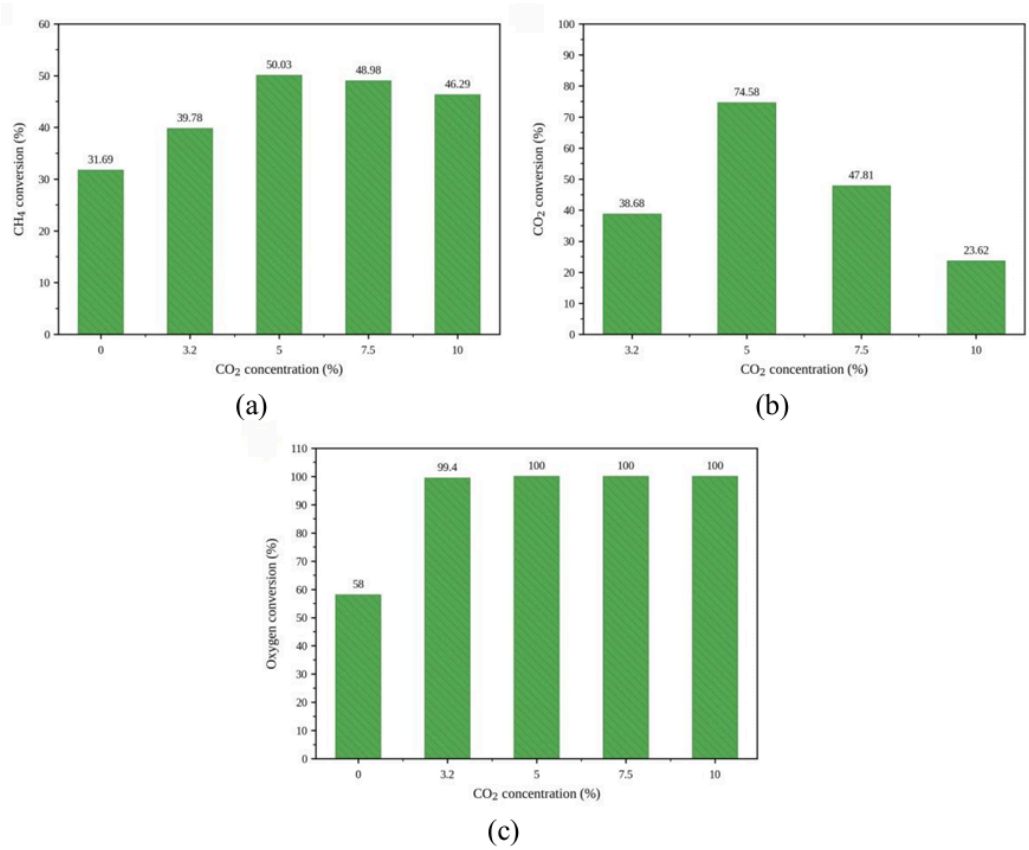


Figure 3. Conversion efficiencies of CH_4, CO_2 and O_2 under different CO_2 concentrations, redrawn from [10]

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The CO_2-assisted LC-CBM test demonstrates that the amount of CO_2 is significant [10]. The addition of CO_2 resulted in an increase in methane conversion up to an intermediate CO_2 concentration, followed by a decrease in methane conversion at higher CO_2 concentrations. The same trend was observed for CO_2 conversion. Thus, it is not a simple continuous improvement, as shown in Figure 3. Dry reforming and carbon removal can be promoted by a moderate CO_2 level. This effect is balanced by additional dilution and modification of the local gas composition at higher levels.

Steam works in a similar way in terms of carbon management. It can support reforming and provide a route for removing deposited carbon. However, low-concentration methane is already diluted. Adding too much steam lowers the effective methane fraction further. The same concern applies to CO_2. The amount added must therefore match the initial fuel composition and the activity of the anode or reforming catalyst.

Fuel adjustment has a practical advantage because it does not require a new anode material. Its limitation is the need for composition control. A fixed steam or CO_2 level may not be suitable when the inlet gas changes. Excess addition can reduce the useful fuel concentration even if it helps carbon removal. For low-concentration methane, steam and CO_2 should therefore be used within a controlled range. Their role is to support reforming and carbon removal, not to replace the main fuel.

5. Conclusion

The most important constraints for SOFCs fueled with low-concentration coalbed methane are low CH_4 content and strong N_2 dilution. They diminish the supply of fuel, limit gas-transport and hinder the conversion of methane. Then there's a second problem: coking. As carbon deposits on Ni, there is less surface available for reaction and the pores are increasingly difficult to traverse by fuel. The conversion of methane and the production of power could then decrease. These three strategies discussed here address different aspects of the problem. Ceria-based materials primarily function to oxidize carbon species associated with Ni but this requires good contact between the phases. A reforming layer is a functional component which will cause a portion of the methane conversion to take place away from the primary Ni–YSZ surface; the added layer is beneficial if it doesn't impede gas flow. When the inlet composition is controlled, steam or CO_2 can help with reforming and carbon removal, but excessive amounts result in a further reduction in the methane fraction. Future tests should be conducted for longer operation times with varying methane mixtures at low concentration rather than only fixed feeds. Methane conversion, electrochemical performance decay, carbon location, pore-structure changes, and interfacial condition should be evaluated together. These results can indicate the effectiveness of a coking-control method with a change in fuel composition.

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