Electrochemically modified, robust solid oxide fuel cell anode for direct-hydrocarbon utilization

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ABSTRACT

A main advantage of solid oxide fuel cells (SOFCs) operating at a high temperature ($> 650\ ^\circ C$) is the flexibility of the fuel they use, specifically as they offer the possibility to utilize methane (natural gas). Unfortunately, however, the state-of-the-art SOFC anodes, composed of a nickel and an anionically conducting oxide such as yttria-stabilized zirconia (YSZ), are associated with Ni-catalyzed carbon deposition and the ensuing degradation of the anode performance. Here, we address these issues through the application of a simple, scalable, cost-effective ceramic coating method known as cathodic electrochemical deposition (CELD). Samaria-doped CeO_2 (SDC) was chosen as the coating material due to its high chemical stability against carbon formation, high electronic and ionic conductivities, and favorable electrocatalytic activity toward fuel oxidation reaction. Nanostructured SDC layers with a high specific surface area were successfully coated onto Ni surfaces via CELD. The physical and chemical attributes of each coating were characterized by a range of analysis tools, in this case SEM, TEM, XRD, EDS, ICP-MS and Raman spectroscopy. An analysis of the AC impedance spectroscopy (ACIS) of Ni-patterned YSZ symmetric cells (anode|electrolyte|anode) with SDC coatings revealed significantly enhanced electrode activity toward fuel oxidation and coking stability under dry or wet methane fuel at $650\ ^\circ C$. These results suggest that the Ni-surface modification via CELD can be a feasible solution for the direct use of hydrocarbon fuels in SOFCs.

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1. Introduction

Fuel cells are electrochemical devices that convert the chemical energy of fuels directly into electricity with high efficiency, overcoming combustion efficiency limitations (e.g. the Carnot cycle) [1]. Although most fuel cells require hydrogen as a fuel, operation on hydrocarbon fuels, and methane in particular, would enable near-term realization of the efficiency advantages even in the absence of a hydrogen delivery infrastructure. Solid oxide fuel cells (SOFCs) hold promise in this regards, in part because of their relatively high temperature of operation (600–$900\ ^\circ C$) [2]. However, the state-of-the-art SOFC anodes, typically cermets composed of nickel and yttria-stabilized zirconia (YSZ), where the former serves as an electronically conducting electrocatalyst and the latter provides the oxygen ion transport pathway, are unsuitable for hydrocarbon electrooxidation because the Ni catalyzes the deposition of graphitic carbon (or "coke"). The deposits not only block access to reaction sites, but also quickly induce mechanical disintegration of the anode [3].

Two key materials strategies have emerged to address the challenge of creating coking resistant SOFC anodes. The first is to replace the Ni with a metal that is catalytically inactive for carbon deposition [4–7], and the second is to replace the entire cermet with a single, mixed ion and electron conducting oxide [8–11]. While both strategies have yielded important successes, neither approach has, as documented in a recent comprehensive review by Ge et al., yielded an SOFC anode with the requisite combination of coking resistance, electrochemical activity and electronic conductivity, to render direct hydrocarbon utilization a technologically attractive proposition [12]. Thus, the field continues to draw considerable attention.

Significantly, the developments to-date hint at future strategies which may bear fruit. In particular, essentially all of the successful demonstrations in the literature of direct hydrocarbon utilization

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in SOFCs, where success is defined here as a peak power density exceeding 100 mW cm^{-2} at 700 °C, involve cermet anodes in which ceria, either doped or undoped, is included as a component [4,5,7,9,13–15]. While ceria is typically not considered in the context of the growing discussion of ceramic anodes, several recent observations suggest that it may be the critical component in high activity, coking-resistant systems. First, under the reducing conditions of an SOFC anode, the electronic conductivity of ceria can easily exceed its already high ionic conductivity [16–18]. Second, samaria-doped ceria (SDC) in particular has a high inherent activity for hydrogen electro-oxidation, such that the reaction pathway is dominated by electrocatalysis on the oxide surface with minimal contributions from the oxide-metal-gas triple-phase boundaries (TPBs), even for structures with reaction site densities approaching those of commercial SOFCs [19]. Moreover, by creating nanostructured ceria with high specific surface area, the activity was enhanced by an order of magnitude, again, in the absence of any contribution from catalytically active metals [20]. Third, beyond electrocatalysis, ceria offers tremendous benefits in terms of high temperature stability (with a melt temperature of 2477 °C) and resistance to carbon deposition (oxidation of reduced ceria by CO_2 yields only CO even at conditions in which carbon is the thermodynamically preferred product) [21–23]. Given these attractive features of ceria (and its doped analogs) it is perhaps not surprising that impregnation of metal/YSZ cermet anodes with ceria has shown promise as a route towards effective direct hydrocarbon SOFCs [24–26]. However, the fabrication methods employed to date, to quote Ge, "appear tedious and costly [12]". For example, Yun et al., had to repeat five series of a 24 h dip-coating and 800 °C calcination step to completely cover a Ni/YSZ electrode with SDC [26]. Moreover, little effort appears to have been directed towards the creation of ceria deposits that display high specific surface area so as to take full advantage of the high electrocatalytic activity of the oxide surface [20,27].

Here, we address these issues through the application of a simple, scalable and cost-effective oxide coating method – cathodic electrochemical deposition (CELD). Electrochemical deposition offers many advantages over other oxide deposition methods such as sputtering, chemical vapor deposition, and pulsed laser deposition because it is performed at ambient temperatures and pressures, achieves high growth rates, requires minimal energy input, and is typically carried out in an environmentally benign aqueous solution using relatively simple salt precursors. Furthermore, there are essentially no limits to the area over which material can be deposited, and film morphology can be varied from extremely smooth to extremely rough through control of the wide range of accessible process parameters, with faster growth rates (obtained at high bias or current density) generally leading to rougher films. These features, along with its long history of industrial application, render it a highly cost-effective and tunable technique. In fact, there have been previous studies using CELD to make dense films of ZrO_2, CeO_2, and doped CeO_2, which may be used as an electrolyte material for SOFC [28–31]. Beyond these generic attributes, the distinct mechanism of CELD suggests additional benefits in the context of SOFC electrodes. In contrast to metal electrodeposition, in which a cationic species is reduced to an insoluble metallic form directly on a growing film, oxide precipitation in CELD occurs as a result of electrogeneration of base, a mechanism described in greater detail below. As a consequence, in addition to supporting film growth, the process can generate nanoparticle precipitates within the solution phase. Freedom from the limitation of growth on conductive substrates opens up the intriguing possibility that CELD can be used to coat the surfaces of composite anode structures in which both electronically insulating and electronically conductive phases are present. Indeed, our preliminary studies provide support for this possibility [32], and

the present work takes advantage of those initial findings.

To avoid the morphological complexities associated with conventional cermet structures, we employ in the present study model composites comprised of patterned Ni thin-films on YSZ single crystal substrates. After an exploration of deposition conditions, in which deposited materials are examined using a broad range of analytical tools, the electrochemical behavior of the most promising films are evaluated by AC impedance spectroscopy (ACIS). We show that just 1 min of CELD treatment creates an oxide coating that enhances activity for hydrogen electrooxidation relative to the uncoated substrate by a factor of 44, and by almost an order of magnitude in the case of methane. We further show that the CELD coated anode has exceptional resistance to carbon deposition.

2. Material and methods

2.1. Cell preparation

Two types of samples were prepared (see Table 1). In the first type, used for CELD optimization and physical characterization, 300 nm-thick Ni films were deposited on (100) single-crystal Si wafers (10 × 10 × 0.5 mm, Siltron) by DC magnetron sputtering (with a DC power of 100 W, a working pressure of 10 mTorr under a flow rate of 30 sccm Ar, and a deposition rate of 60 nm min^{-1}). The second type of sample was used for electrochemical characterization. Ni electrodes were applied in a symmetric arrangement on both sides of a (100) single crystal YSZ (8 mol%, 10 × 10 × 0.5 mm, MTI Corp.) substrate, which serves as an oxygen-ion conductive electrolyte. The YSZ electrolyte was partially exposed by patterning the 300 nm thick Ni into connected strips in which the Ni width and exposed YSZ width were equal (Table 1 and Fig. S1). Ni patterning was achieved using a photolithographic lift-off process. A positive photoresist (AZ4562) was spin-coated onto the YSZ substrate at 4000 rpm. Next, the samples were aligned by a photomask in a contact aligner and exposed to UV light for 55 s. The Ni layer was sputtered by DC magnetron sputtering with deposition conditions identical to those above. Metal lift-off was achieved by immersing the samples in acetone at room temperature and subjecting them to ultrasonification. Electrochemical measurements were performed using Ni strip widths of 10, 20, 40 and 80 μm, corresponding to triple-phase boundary densities ranging from 85 to 645 cm cm^{-2}. A few additional patterns (of slightly differing geometries) were examined to explore ceria deposition behavior.

2.2. Electrochemical deposition

For both types of samples, SDC layers were applied by CELD using a standard three-electrode system (Fig. 1(a)) comprised of the deposition substrate as the working electrode (held in place using tailor-made aluminum clips), a counter electrode (carbon

Table 1
Two types of samples were prepared in this work. One for CELD optimization and physical characterization (Type 1, Ni|Si substrate) and the other for electrochemical characterization (Type 2, patterned Ni|YSZ substrate|patterned Ni).

Type	Substrate	Name	Ni width [μm]	Ni–Ni distance [μm]	3PB length [cm/cm²]	2PB area [cm²/cm²]
1	Si (100)			No patterns		
2	YSZ (100)	10–10	10	10	644.8	0.32
		20–20	20	20	324.8	0.32
		40–40	40	40	164.8	0.32
		80–80	80	80	84.8	0.32