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# $H_2$ oxidation pathways on Ni-ceria surface by electrical conductivity relaxation method

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## ABSTRACT

The reaction of $H_2$ oxidation on samaria-doped ceria (SDC) surface deposited with scattered Ni particles is studied utilizing the electrical conductivity relaxation method. The surface reaction rate is remarkably improved by the Ni particles. The improvement linearly increases, but is not directly proportional to the length of Ni-SDC-gas boundary (3 PB), suggesting there are three pathways for the $H_2$ oxidation, the original reaction on bare SDC-gas (2 PB) interface, the reaction through 3 PB and the 2 PB reaction with hydrogen atoms migrating from Ni surface via spillover. The original 2 PB reaction contribution decreases significantly from 100% for the bare SDC to 13% after Ni deposition and further to 3% at the Ni particle density of 417 $\mu m^{-2}$. Meanwhile, the Ni related reaction from 3 PB and 2 PB spillover contributes up to 97%, demonstrating that Ni can greatly accelerate the $H_2$ oxidation reaction. The 3 PB contribution decreases while the 2 PB spillover contribution increases with the increase of the average Ni particle distance, i.e. the decrease of 3 PB length and number of Ni particles per surface area. The 3 PB and 2 PB spillover contributes almost equally when the average distance is 76 nm and particle density is 66.1 $\mu m^{-2}$. The results show the reaction on Ni-SDC could be dominated by both 3 PB and 2 PB spillover pathways. The 2 PB spillover may dominate the total reaction for model patterned electrodes and the 3 PB should control hydrogen reaction for nanostructured electrodes fabricated by impregnation method.

## 1. Introduction

Ceria participates in a number of industrially attractive applications involving $H_2$ formation or dissociation such as ethanol steam reforming, the water-gas shift reaction and anodic oxidation in solid oxide fuel cells (SOFCs) [1–4]. Ceria surface plays a central role in these reactions since it can efficiently promote the reaction rates, often in conjunction with supported or dispersed metals [5]. A large majority of computational studies and electrochemical experiments are thus conducted, however, the exact reaction mechanisms even for the simple hydrogen oxidation at SOFC anodes are not fully understood yet [6]. Density functional theory calculations have identified the minimum energy paths for $H_2$ oxidation on the $CeO_2(111)$ surface in the atomic level [7,8]. In experimental analysis, the ceria or doped ceria surface hydrogen oxidation reaction sites can be estimated in macro level, but still in the discussion. It has been demonstrated through the electrochemical impedance analysis on ceria-metal (Pt, Ni) constructions with patterned electrodes that the anode hydrogen oxidation reaction is dominated by the ceria-gas 2 PB interface while the contribution of ceria-metal-gas three phase boundary (3 PB) is negligible [9]. On the contrary, investigation using electrical conductivity relaxation has shown that the addition of Pt on the doped ceria surface could significantly enhance the rate of $H_2$ oxidation which mostly takes place at the 3 PB [10]. The results from single cell measurement suggest that the peak power density increases with 3 PB length while not obviously affected by the 2 PB interface [11]. Among various metal-ceria cermets, Ni-ceria is the widely investigated anode, which is capable of directly using hydrocarbon fuels. The oxidation reaction via metal-ceria anodes is much more complicated than the traditional Ni-YSZ (yttria-stabilized zirconia) anode due to the mixed ionic-electronic conductivity properties of ceria under reducing atmospheres. For Ni-YSZ, the electrochemical reactions distinctly happen at the YSZ-Ni-gas 3 PB which are realized by hydrogen spillover [12]. The reactions are believed to happen on ceria-gas 2 PB interface in addition to 3 PB when the cermet anodes are composed of ceria and doped ceria [13].

This work tries to figure out the $H_2$ oxidation pathways on Ni-SDC (samaria doped ceria) by means of electrical conductivity relaxation (ECR). The global $H_2$ oxidation via doped ceria is given by Kroger-Vink notation [9].

$$H_2(g) + O_O^{\times} \rightarrow H_2O(g) + V_O^{\cdot\cdot} + 2e' \tag{1}$$

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where $V_O^{\cdot\cdot}$ represents a doubly ionized oxygen vacancy, the majority ionic carrier in doped ceria. The $H_2$ oxidation rate is the same as the reduction rate of $Ce^{4+}$, which is also the surface reaction rate that can be determined by ECR method through the concentration change of oxygen vacancy in the solid state ceria. According to the linear interface kinetics assumption [14], the rate $r$ (mol s$^{-1}$) can be expressed as

$$r = Sk_{chem}\left[C(t) - C(\infty)\right] \tag{2}$$

where $k_{chem}$ (cm s$^{-1}$) is the rate constant, often referred as the chemical surface oxygen exchange coefficient that can be obtained from ECR tests. $S$ (cm$^2$) is the surface area, $C(t)$ (mol cm$^{-3}$) presents the oxygen concentration at time $t$, and $C(\infty)$ (mol cm$^{-3}$) presents the concentration for equilibrium state to the final hydrogen partial pressure. The reaction rate $r$ and rate constant $k_{chem}$ are discussed with respect to 2 PB area and 3 PB length to figure out the contribution of various pathways.

## 2. Experimental

SDC ($Sm_{0.2}Ce_{0.8}O_{1.9}$) powder was prepared using the carbonate co-precipitation method with cerium nitrate hexahydrate ($Ce(NO_3)_3{\cdot}6H_2O$, ≥99.9%), samarium nitrate hexahydrate ($Sm(NO_3)_3{\cdot}6H_2O$, ≥99.9%) and ammonium carbonate ($(NH_4)_2CO_3$, ≥99.9%) as the precursors [15]. All the chemicals were from Sinopharm Chemical Reagent Co., Ltd. The SDC powder was heated at 600 °C for 2 h. The powder was uniaxially dry-pressed under 320 MPa into rectangular bars, which were subsequently annealed in air at 1500 °C for 5 h with a ramping rate of 3 °C min$^{-1}$. The SDC bars were about 30.0 mm long, 5.10 mm wide, and 0.50 mm thick. Ni particles are formed using a sputter-heating process. The sputtering was conducted to deposit Ni film on the SDC bar surface with a nickel target (4N purity, Kejing Materials Technology Co. Ltd.) using sputter coater (JFC-1600, JEOL) at 20 mA and under the vacuum of 8 Pa. Afterwards, the sample was heated at 800 °C for 2 h with a ramping rate of 3 °C min$^{-1}$ in reducing atmosphere (10% $H_2$ with Ar as the carrier gas) to convert the Ni film to Ni particles. The deposition time was set to be 10–160 s to vary the film thickness and consequently, the amount of Ni particles per unit area. The 2D microstructures and 3D topography of the surface were revealed using scanning electron microscopy (SEM, JSM-6700F, JEOL) and atomic force microscope (AFM, INNOVA, VEECO). The area covered by the Ni particles and the length of Ni-SDC boundary (the Ni-SDC-gas 3 PB) were statistically determined using ImageJ. Electrical conductivity relaxation (ECR) method was utilized to characterize the $H_2$ oxidation reaction at 800 °C with a digital multimeter (2001-785D, Keithley) using the four-point technique. $H_2$—Ar gas mixtures were used and the gas atmosphere was changed from flowing 5% $H_2$ to 10% $H_2$ for $H_2$ oxidation. The gas was humidified using a moisture bottle, resulting in about 3% water vapor.

## 3. Results and discussion

Fig. 1 is the SEM micrographs for the surface microstructures of the Ni-SDC bars used for the ECR measurements and the three-dimensional AFM topography. Fig. 1a shows that the SDC bar is fully dense, no holes or cracks are observed. The relative density is 97.9% of the theoretical value as determined using the Archimedes method. The density is high enough for the ECR test [16]. The average grain size is about 2.5 μm. The small particles on the SDC grains are nickel as formed in the sputtering-heating processes, in which the sputtering results in thin nickel films while the heating turns the films into particles. The Ni particles are evenly distributed, not connected to each other. The bar conductivity should not be affected since no connections are formed among these Ni particles. The particle number per unit area increases with the sputtering time while the diameter of Ni particles does not change much, from 0.04 μm to 0.03 μm. The average distance between two Ni particles is reduced to < 10 nm when the deposition time increases to 160 s. Fig. 1d shows the micrograph of atomic force microscope (AFM) for Ni deposited in 20 s. The average height of Ni particles is 5.4 nm. SEM graphs are statistically analyzed using Image J to obtain the Ni surface coverage $\theta$ which is defined as Ni area per unit SDC area, the ceria-gas 2 PB area $1-\theta$, the Ni-SDC-gas 3 PB length per unit area $L_{3PB}$ (μm$^{-1}$), average distance between Ni particles $d$ (μm) and the particle numbers per unit area $n$ (μm$^{-2}$), Table 1.

Fig. 2a shows the conductivity data plotted as a function of time. In the initial atmosphere, 5%$H_2$-3%$H_2O$-92%Ar, the conductivity of bare SDC is 0.17 S cm$^{-1}$, which is consistent with those reported in the literature [17]. When the gas component is switched from 5%$H_2$–3%$H_2O$-92%Ar to 10%$H_2$–3%$H_2O$-87%Ar, oxygen ion releases from SDC lattice, producing additional charge carriers, i.e. oxygen vacancies and electrons, accompanied with the valence change of ceria from $Ce^{4+}$ to $Ce^{3+}$. As a result, the conductivity increases with the decrease of oxygen ion concentration from 0.17 to 0.21 S cm$^{-1}$. After Ni deposition, the conductivity is almost the same for all samples, demonstrating that the Ni particles have negligible effect on the conductivity since these particles are not connected to each other. Fig. 2b shows the normalized conductivity data as a function of time. For the bare SDC, the relaxation time is about 7000 s. When Ni particles modify the surface, the time is remarkably reduced to < 1200 s, suggesting that Ni can significantly accelerate the surface reaction rate. The rate constant, i.e. the surface exchange coefficient $k_{Ni\text{-}SDC}$, can be calculated from the normalized conductivity curves as shown in Fig. 2b [18].

Hydrogen oxidation on ceria consists generally of five steps, as schematically shown as Pathway I in Fig. 3a [19], including 1) hydrogen molecules adsorb on the surface with a minimum energy where $H_2$ lies on top of a $Ce^{4+}$ site, 2) hydrogen dissociation proceeds by forming a bidentate Ce-H-H-O configuration, 3) the H—H bond breaks through the polarization of binding to the surface O atom with an energy barrier of 0.38 eV, transferring to the ceria surface one electron that reduces one Ce atom, and the two H atoms bind to a Ce and to an O atom, respectively, leading to the formation of $Ce^{3+}$—H and O—H surface group, 4) H atom migrates from Ce to O site with a further energy barrier of 0.29 eV, and 5) two O—H groups form a $H_2O$ molecule followed by $H_2O$ desorption and leaving an oxygen vacancy. The first four steps result in $H_2$ dissociation and O—H group formation with a total energy barrier of 0.99 eV.

The surface reaction rate on the bare SDC, $r_{SDC}$, can be calculated

$$r_{SDC} = k_{SDC}S\left[C(t) - C(\infty)\right] \tag{3}$$

where $k_{SDC}$ is the rate constant for bare SDC, $1.42 \times 10^{-5}$ cm s$^{-1}$ as calculated from the relaxation profile.

When SDC surface is deposited with Ni particles, the reaction rate $r_{Ni\text{-}SDC}$ is

$$r_{Ni-SDC} = k_{Ni-SDC}S\left[C(t) - C(\infty)\right] \tag{4}$$

where $k_{Ni\text{-}SDC}$ is the chemical surface exchange coefficient derived from the relaxation result, Table 1. It was $39.4 \times 10^{-5}$ cm s$^{-1}$ when the sputtering was conducted for 160 s. $r_{Ni\text{-}SDC}$ is contributed by two parts. One is the SDC surface reaction that is not related to Ni particles, Pathway I. The rate is $r_{SDC}(1-\theta)$, considering reasonably that the non-Ni-related reaction taken place on Ni-SDC is the same as that on the bare SDC. The other is Ni related reaction, $r_{Ni}$, the rate is expressed as

$$r_{Ni} = r_{Ni-SDC} - r_{SDC}(1-\theta) \tag{5}$$

Meanwhile,

$$k_{Ni} = k_{Ni-SDC} - k_{SDC}(1-\theta) \tag{6}$$

where $k_{Ni}$ is the surface exchange coefficient caused by Ni particles. When Ni particles are deposited on the SDC surface, $H_2$ can be easily dissociated to H atoms on Ni surface. And for a single H atom, the adsorption on-top of a O site is the lowest energy configuration [8,19]. Therefore, hydrogen oxidation at 3 PB may include the following steps [20]: 1–3) $H_2$ adsorption and disassociation to H atoms on Ni with an energy barrier of ~0.1 eV, 4) H migration to a surface oxygen atom near