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Atomic layer deposition of highly dispersed Pt nanoparticles on a high surface area electrode backbone for electrochemical promotion of catalysis

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ABSTRACT

A novel catalyst design for electrochemical promotion of catalysis (EPOC) is proposed which overcomes the main bottlenecks that limit EPOC commercialization, i.e., the low dispersion and small surface area of metal catalysts. We have increased the surface area by using a porous composite electrode backbone made of (La_{0.8}Sr_{0.2})_{0.95}MnO_{3-δ}/Ce_{0.9}Gd_{0.1}O_{1.95} (LSM/GDC). Highly dispersed Pt nanoparticles with an average diameter of 6.5 nm have been deposited on LSM/GDC by atomic layer deposition (ALD). This novel design offers, for the first time, a controllable and reproducible method for the fabrication of EPOC catalysts. The bare electrode backbone shows negligible activity for propane oxidation, while in the presence of Pt nanoparticles a high catalytic activity is obtained above 200 °C. The performance of the Pt-loaded LSM/GDC catalyst was significantly improved by application of small currents ($I < 500 \mu\text{A}$), leading to a 27–33% increase as a function of the open circuit catalytic rate, with apparent Faradaic efficiency values ranging from 1000 to 3860% at 300 °C. Our results demonstrate that EPOC is a valid approach for enhancing the catalytic activity of nano-structured catalysts.

1. Introduction

The approach known as electrochemical promotion of catalysis (EPOC) refers to the pronounced reversible and controlled changes in catalytic properties (activity and selectivity) that occur upon electrical polarization [1–4]. Since the discovery of the effect [5], > 100 different catalytic systems have been electrochemically promoted on various metal catalysts supported on different ionic conductors [1–6].

EPOC studies employ an electrochemical cell in which one of the electrodes is the catalyst for the reaction under study. By controlling the polarization, ions can be pumped towards or away from the catalyst, changing its work function and thus its catalytic properties [1–6]. Despite the apparent advantages of this system, such as controlling the coverage of the promoting ions in situ, EPOC has not yet had any industrial applications, mainly due to its much lower activity per catalytic mass compared with classic nano-dispersed powders [2,7–12]. Therefore, in the last few years, EPOC research has been focused on

overcoming this issue, which would help advance the scaling up of the concept [2,7–17].

The most promising EPOC catalyst design has been reported by Kambolis et al., in which Pt nanoparticles have been deposited by wet impregnation into a porous LSCF/GDC (La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ}/Ce_{0.9}Gd_{0.1}O_{1.95}) electrode [10]. This design was inspired by solid oxide electrolyte cells (SOEC) [18], with the porous nature of LSCF/GDC offering a higher surface area than conventional pure metallic films. In addition, LSCF mainly plays the role of an electron conductor while GDC is an ionic conductor [19], so the combination provides the two functionalities that are important for electrocatalysis [1–4]. The aforementioned approach resulted in highly dispersed Pt nanoparticles of 3–20 nm with an average size of 8 nm. However, wet impregnation constitutes a poor technique in terms of reproducibility and control of the particle load and its size distribution. In this study we propose a more reliable method, i.e. atomic layer deposition (ALD), aimed at overcoming the limitations outlined above.

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ALD is a thin film deposition technique based on the chemical reaction of gas phase species on a solid surface. ALD is currently used commercially by the semiconductor industry and thin-film magnetic head industry. There has also been recent interest in using ALD in other application areas, such as photovoltaics and organic electronics. ALD is performed by the sequential exposure of the substrate to two (or more) different gas species separated in time by purging steps. Each gas species reacts with the substrate up to saturation, through a self-limiting reaction mechanism. Because of its self-limiting nature, the main advantages of ALD are the control of film thickness at the atomic scale, high conformity with surface features and high reproducibility [20–26]. On most metal oxides, ALD generally starts with the growth of small islands (i.e. nanoparticles) and many ALD cycles are required to obtain a completely closed film. Therefore, ALD is ideal for accessing and decorating the entire volume of our porous electrode backbone with Pt nanoparticles.

The aim of this study is to investigate the electro-promotion of propane oxidation over highly dispersed Pt nanoparticles prepared by ALD. The electrode backbone in which Pt nanoparticles are deposited is a porous $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.95}\text{MnO}_{3.8}/\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (LSM/GDC) composite, which offers mixed ionic–electronic conductivity. 100 Pt ALD cycles were selected based on literature studies of Pt deposition on flat Al_2O_3 substrates in which 100 cycles resulted in Pt nanoparticles with an average size of 4.5 nm [22].

2. Experimental

2.1. Cell preparation and characterization

Two commercial partial cells (FuelCellMaterials) with a 50 μm LSM/GDC composite electrode (50%–50%, 17 mm diameter) deposited on a 150 μm Hionic™ electrolyte support (20 mm diameter) were employed in the present study. One was used as a reference cell, while the second was dedicated to the Pt ALD case study.

Two gold films were deposited on the opposite side of the Hionic™ pellet, to act as counter and reference electrodes, respectively. Gold was selected due to its negligible catalytic activity in propane oxidation, as verified through blank experiments under experimental conditions. An electrochemical workstation Voltalab PGP 201 (Radiometer) was used to apply and measure both potential and current. The catalyst potential ΔU_{WR} was measured between the working electrode (Pt-LSM/GDC) and the reference electrode (Au).

Pt was deposited on the porous LSM/GDC by ALD using a home-made deposition system described in detail elsewhere [24]. The base pressure of the reactor was $< 10^{-6}$ mbar. MeCpPtMe_3 (98% from Sigma Aldrich) was used as precursor and O_2 gas at 1 mbar as reactant. The precursor was contained in a stainless steel cylinder, heated at 30 °C, and brought into the reactor using Ar as carrier gas. The lines from the precursor to the reactor were heated to 50 °C and the reactor wall to 90 °C. The ALD recipe starts by dosing MeCpPtMe_3 for 4 s, then using 3 s of Ar to purge the precursor line, followed by 3 s of pumping down. Then O_2 gas is dosed for 10 s and afterwards the reactor is pumped down for 10 s. The deposition was carried out with the substrate holder maintained at 300 °C. The ideal procedure for Pt ALD deposition on LSM/GDC is shown in Fig. 1(a).

2.2. SEM and TEM microscopy

A cross-sectional sample for transmission electron microscopy (TEM) analysis was made by means of standard focus ion beam (FIB) lift-out sample preparation and SEM images by an FEI Nova 600 Nanolab SEM/FIB. Prior to FIB milling, a stack of protective layers consisting of SiO_2 and Pt was deposited in the FIB. Subsequent TEM studies were performed using a JEOL ARM 200 probe corrected TEM, operated at 200 kV, equipped with a 100 mm² Centurio SDD EDS detector.

2.3. Catalytic activity measurements

The design of the experimental setup has been described in detail elsewhere [6,13]. The reactant gases were certified mixtures of 0.80, 5.0 and 99.999% C_3H_8 , O_2 and He (Air Liquide), respectively. The analysis of reactants and products was carried out by online gas-chromatography (R3000 micro-GC SRA instruments) and IR spectroscopy (Horiba VA3000).

Under closed circuit conditions, the cell-reactor could operate as an electrochemical oxygen “pump”. Using an external power source, a current, I , can be imposed through the oxygen-ion (O^{2-}) conducting solid electrolyte, which corresponds to an oxygen-ion flux of $I/2F$. In order to quantify the EPOC, Vayenas and co-workers [1] have defined two dimensionless parameters, apparent Faradaic efficiency, Λ , and rate enhancement ratio, ρ , as follows:

$$\Lambda = (r - r_0)/(I/nF) \quad (1)$$

$$\rho = r/r_0 \quad (2)$$

where r is the closed-circuit reaction rate (i.e. under polarization) and r_0 is the open-circuit reaction rate (i.e. at $I = 0$) and I/nF is the imposed flux of O^{2-} , where n is the number of exchanged electrons.

3. Results and discussion

Analysis of the Pt nanoparticles deposited on the porous LSM/GDC is not a trivial task. In our previous work [10] we employed an extractive replica technique for TEM analysis of the Pt nanoparticles, which involves electrode crushing and the dissolution of the electrode backbone in a hydrofluoric acid solution. In order to gain further insight into the distribution of Pt on the electrode backbone, we conducted a TEM analysis on a cross-section of an electrode (after catalysis). Fig. 1(b,c) shows SEM images of the electrode surface before and during FIB preparation of the TEM lamella.

A High Angle Annular Dark Field (HAADF)–scanning TEM image of the entire TEM lamella is displayed in Fig. 1(d). In this sample three sites of interest have been denoted as P1, P2 and P3. TEM images of these areas are shown in Fig. 1(e–g). The presence and distribution of the Pt particles can be clearly discerned. Because of the different inclinations of the grain surfaces with respect to the imaging direction, both vertical and lateral dimensions of the Pt particles can be imaged.

ImageJ software was used to determine the Pt particle size distributions, which for areas P1 and P2 are presented in Fig. 1(h,i) and for the entire lamella area in Fig. 1(j). The Pt nanoparticles have a uniform distribution with a particle size range of 3–10 nm and an average size of 6.5 nm. Considering hemi-spherical Pt nanoparticles, one can estimate a Pt dispersion of 18.2% [27]. Particle size analysis was performed after catalytic evaluation. It is well known that the particle size might increase after catalysis due to agglomeration [28]. Moreover, the growth of the nanoparticles is influenced by the substrate [22]. Taking this into account, the average Pt particle size of 6.5 nm after 100 ALD cycles is not too far from the reported value of 4.5 nm on Al_2O_3 [22].

In order to evaluate the catalytic performance of the Pt nanoparticles deposited on the LSM/GDC support, light-off experiments were performed on both the Pt-LSM/GDC (without involving a pre-reduction step for Pt) and bare LSM/GDC samples (Fig. 2(a)). The temperature was increased from ambient to 425 °C with a heating rate of 2 °C/min. Fig. 2(a) shows the CO_2 production rate and the C_3H_8 conversion as a function of temperature. It can be seen that the LSM/GDC support was totally inactive for propane oxidation, while the addition of the Pt nanoparticles strongly increased the catalytic activity. For the Pt-loaded sample, the conversion of propane was shown to increase rapidly after 200 °C and reach 23% at 425 °C.

The impact of various polarizations between -1.0 V and $+1.0$ V on the catalytic performance of the Pt-free LSM/GDC sample was investigated at 300 °C, and no modification of the propane conversion

Fig. 1. (a) Schematic representation of Pt deposition on the porous LSM/GDC electrode backbone using ALD. (b) and (c) SEM images of the surface of the Pt-loaded LSM/GDC, displaying the location of the cross-section. (d) HAADF-STEM image of the TEM lamella. The sample is covered by a stack of protective SiO₂/Pt layers. (e), (f) and (g) HAADF-STEM images of the Pt-loaded LSM/GDC at three different points of interest. (h), (i) and (j) show the corresponding size distributions at two points and in the overall lamella.

was observed. On the other hand, the Pt-loaded LSM/GDC exhibited non-Faradaic behavior under both positive and negative polarizations. For instance, Fig. 2(b) displays the impact of three consecutive steps of small positive currents ($I = 300, 500$ and $100 \mu\text{A}$) on the catalytic rate of CO₂ production at 300°C . The rate of propane oxidation gradually increases from $2.20 \times 10^{-8} \text{ mol CO}_2\text{s}^{-1}$ and reaches a steady-state value at $2.88, 2.93$ and $2.79 \times 10^{-8} \text{ mol CO}_2\text{s}^{-1}$, i.e. a rate enhancement of 131, 133 and 127% ($\rho = 1.31, 1.33$ and 1.27) respectively. The apparent Faradaic efficiency, Λ , was found to be 14.6, 10.0 and 38.6, respectively, for the three different applied currents. Thus, the catalytic activity is up to 38.6 times higher than that predicted by Faraday's law, considering electro-oxidation of propane with oxygen ions. After interruption of the current the reaction rate returned slowly to its open-circuit value, indicating the reversibility of EPOC.

The increase in the reaction rate observed under positive polarization can be explained on the basis of the rules of electrochemical promotion [29]. It has been established that the supply of an electro-negative ion, such as O^{2-} , to the catalyst-electrode surface, weakens the Pt–O bonds and therefore increases its work function [1–4]. The latter leads to the improved chemisorption of propane, which is known to be linked with the rate-determining step for propane oxidation [30,31]. After current interruption, the O^{8-} promoters are consumed and therefore the catalyst returns to its initial state over time [29,30]. The moderate values of the rate enhancement ratio and Faradaic efficiency can be attributed to the pre-activation of the Pt nanoparticles due to their size via self-driven spillover [1–3]. In addition, only a minor part of the current applied between the LSM/GDC electrode and the counter electrode probably passes across the Pt nanoparticles.

Fig. 2. (a) Comparison of catalytic (open-circuit) performance for propane combustion using Pt-LSM/GDC and bare LSM/GDC support. (b) Effect of positive and (c) negative currents on the potential and CO₂ formation. (d) EPOC stability test under positive polarization. $P_{\text{C}_3\text{H}_8}/P_{\text{O}_2} = 0.22 \text{ kPa}/2.2 \text{ kPa}$, $T = 300^\circ\text{C}$, $F_t = 100 \text{ ml min}^{-1}$ (NTP).

On the other hand, the removal of O²⁻ from the Pt-loaded sample (negative current application of -300 and $-500 \mu\text{A}$) had a poisoning effect on the catalyst, which also resulted in non-Faradaic modification of the catalytic rate (Fig. 2(c)) in good agreement with literature [10,29]. Interestingly, the poisoning effect was limited to 74% of the initial reaction rate and a Faradaic efficiency of 12.0. Application of an even higher negative current ($I = -500 \mu\text{A}$) did not change the catalytic rate; this demonstrates a saturation effect, which can be attributed to the current bypassing the Pt nanoparticles. In other words, the application of a higher negative current cannot affect the performance of the Pt nanoparticles, since the extra current (i.e. oxygen pumping) takes place on Pt-free areas of the LSM/GDC surface.

Finally, the stability of the phenomenon was verified by a long-term experiment applying a current of $100 \mu\text{A}$ (Fig. 2(d)). The performance of the catalyst is relatively steady since the CO₂ production rate decreases only slightly from 2.78 to $2.73 \times 10^{-8} \text{ mol CO}_2 \text{ s}^{-1}$ after 13 h of polarization. This indicates that possible agglomeration of Pt nanoparticles during the TPO treatment at a higher temperature (i.e. 425°C) has resulted in a stable catalyst configuration.

4. Conclusions

The combination of ALD with SOEC technological advances led to a Pt-decorated composite electrode, which was successfully employed for the electropromotion of propane combustion. In the implemented design, the three functionalities (i.e. catalytic activity, electronic and ionic conductivity) needed for efficient EPOC catalysts are separated into three phases (i.e. Pt, LSM and GDC). The moderate magnitude of electrochemical promotion can be attributed to the pre-activation of the Pt nanoparticles due to their small size via self-driven spillover or current by-pass. Future plans aimed at enhancing the magnitude of the effect will be directed towards tuning either the Pt loading and/or the electronic conductivity of the electrode backbone.

Utilization of the ALD technique brings EPOC systems one step closer to commercialization due to minimized catalyst loadings. In view

of the possible practical application of EPOC, the success of our concept should be verified with reactions of industrial importance, where modifications in product selectivity can also occur.

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