



# 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<sub>0.8</sub>Sr<sub>0.2</sub>)<sub>0.95</sub>MnO<sub>3.8</sub>/Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>1.95</sub> (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<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3.8</sub>/Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>1.95</sub>) 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 (La<sub>0.8</sub>Sr<sub>0.2</sub>)<sub>0.95</sub>MnO<sub>3-δ</sub>/Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>1.95</sub> (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<sub>2</sub>O<sub>3</sub> 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 Δ*U*<sub>WR</sub> 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<sup>−6</sup> mbar. MeCpPtMe<sub>3</sub> (98% from Sigma Aldrich) was used as precursor and O<sub>2</sub> 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<sub>3</sub> for 4 s, then using 3 s of Ar to purge the precursor line, followed by 3 s of pumping down. Then O<sub>2</sub> 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<sub>2</sub> 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 mm<sup>2</sup> 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<sub>3</sub>H<sub>8</sub>, O<sub>2</sub> 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<sup>2−</sup>) conducting solid electrolyte, which corresponds to an oxygen-ion flux of *I*/2*F*. 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*<sub>0</sub> is the open-circuit reaction rate (i.e. at *I* = 0) and *I*/n*F* is the imposed flux of O<sup>2−</sup>, 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<sub>2</sub>O<sub>3</sub> [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<sub>2</sub> production rate and the C<sub>3</sub>H<sub>8</sub> 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

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