



# Atomic layer deposition in the preparation of Bi-metallic, platinum-based catalysts for fuel cell applications

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## ABSTRACT

Atomic layer deposition (ALD) is a thin layer synthesis method applied in this study for preparing carbon-supported mono-metallic Pt- and bi-metallic PtCo catalysts. The catalyst characterization confirmed that small metal particles with a narrow particle size distribution and high metal dispersion were obtained. The location of the metals on the surface was controlled by alternating the ALD cycles, and the formation of bi-metallic PtCo particles on the support was observed. The prepared catalysts proved to be active for methanol oxidation and oxygen reduction in an acidic media. In addition, the durability of the catalysts in electrochemical oxidation was enhanced by varying the metal cycle order in the catalyst preparation. After the deposition of Co on the catalyst, one ALD cycle of Pt favored the catalyst durability in the methanol oxidation reaction.

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## 1. Introduction

Atomic layer deposition (ALD) is a solvent-free method for preparing catalysts by adding gaseous metal precursors to a solid surface. Under proper conditions, the metal precursors will attach themselves to the substrate surface by chemisorption and saturate it. This method has been widely used for preparing different thin films [1,2]; however, it can also be applied for catalyst preparation. ALD has been used to prepare catalysts with various supports, for example carbon-supported catalysts with metals like Pt [3], Pd [4,5], and Ru [6]. ALD has also been used for bi-metallic catalysts and thin films, for example to prepare Pt–Pd on Al<sub>2</sub>O<sub>3</sub> [7], Ru–Pt thin films on SiO<sub>2</sub> [8], and Pt–Ir on SiO<sub>2</sub> [9]. ALD is an advantageous preparation method because it results in small metal particles with a narrow particle size distribution [4,5,10] and high metal dispersion [7] when compared to traditionally used impregnation methods. Moreover, ALD is especially interesting for bi-metallic catalysts because the availability of the metals on the catalyst surface can be controlled based on the order of the metal cycles in the ALD process.

Metal loading is one of the key parameters that define the activity of the supported heterogeneous metal catalysts. The loading can be controlled in various ways using different preparation methods. For example, with impregnation methods the metal loadings are controlled by the amount of metal precursor used [11], whereas with the ALD method they are controlled by precursor evaporation and surface temperature, by the number of precursor feed cycles, and by the surface sites on the catalyst support [12]. Another important feature of catalyst preparation is the metal crystal phase, which is typically controlled by the catalyst treatment performed after metal addition, like calcination or reduction. Reduction in particular is used to reduce the active metals to a metallic state on the catalysts [13]. Similar to the impregnation methods, with the ALD process different kinds of oxidation and reduction treatments after the precursor feed are used to remove ligands from the precursor and to obtain the desired metal oxidation state. Typically, an oxidation treatment with water, oxygen, or ozone is used most often in ALD to remove the ligands, especially in thin film applications [14]. ALD is a modification of chemical vapor deposition (CVD). The main difference between these methods is that in ALD the precursor reactions in gas phase are prevented by feeding the different precursors separately [14].

The properties of the catalyst—particle size, metal loading, metal distribution, and surface structure—play a key role in important electrocatalytic reactions, such as methanol oxidation (MOR) [15]

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or oxygen reduction (ORR) [16]. These two reactions have been intensively studied due to their importance in fuel cell applications. The MOR is mostly studied on Pt-based catalysts [17] and the electrocatalytic oxidation of methanol on Pt is extremely dependent on such factors as surface crystallography [18,19] and particle size [20]. The desirable situation for highly efficient direct methanol fuel cell (DMFC) would be maximum methanol oxidation at low overpotentials. However, on Pt the strongly bonded CO intermediate hinders the MOR and causes a low current efficiency for CO<sub>2</sub> formation. A convenient way to modify the properties of the Pt catalyst and overcome this situation is to make alloys or bi-metallic surfaces [21]. Of the several bi-metallic catalysts that have been studied for methanol oxidation [22–24], researchers report that PtRu is the most active in terms of methanol oxidation. However, the high cost and limited supply of Ru has directed research in the direction of an alloying Pt with 3d transition metals, such as Co, Ni, and Fe. For the particular case of PtCo, the addition of Co promotes the onset potential of methanol dehydrogenation, thereby increasing the catalytic performance of the MOR compared to that of the mono-metallic Pt catalyst [25].

On the other hand, the cathode reaction in both polymer electrolyte fuel cells (PEFC) and DMFC is ORR. The kinetic limitations of this reaction lead to cell voltage losses, and developing new and better catalysts for this reaction would be a key way to improve PEFC. Considerable progress has been made on Pt-based, bi- and tri-metallic electrocatalysts, such as alloying Pt with 3d-transition metals, including Fe, Co, Ni [26], Cu [27], Cr [28], and Mn [29]. Of these catalysts, PtCo systems have received considerable attention because of their relatively high level of ORR activity and stability in acidic environments [30–32]. However, the reaction activity strongly depends on the ratios between the metals and the structure of the particles.

The aim of this paper was to study the ALD method for preparing carbon-supported, bi-metallic PtCo catalysts. Several catalyst batches were prepared in order to study the mechanism of bi-metallic particle formation on different metal loadings. Moreover, with the aim of increasing the stability of the PtCo catalysts, subsequent cycles of Pt were deposited on the initial PtCo catalyst. The physical characterization of the catalysts was performed by atomic emission spectroscopy (AES), X-ray diffraction (XRD), high-resolution transmission electron microscopy (HR-TEM), X-ray photoelectron spectroscopy (XPS), and CO chemisorption. Electrochemical characterization using cyclic voltammetry was also conducted to help physically characterize the ALD-prepared catalysts. Moreover, the catalytic activity for both MOR and ORR was evaluated.

## 2. Experimental

### 2.1. Catalyst preparation

The ALD catalyst preparation was carried out in a commercial, flow-type, F-120 ALD reactor (ASM Microchemistry) operating at a reduced pressure of 0.5–1 kPa. As a catalyst support material, commercial carbon black (Vulcan XC72R, Cabot GR-3875) was used as received with no further modifications. Before initiating the ALD precursor cycle, the support material was pretreated by drying in an N<sub>2</sub> flow (AGA, 99.999%) at 180 °C for 5 h. The metal precursors, the Pt precursor, platinum acetyl acetonate, Pt(acac)<sub>2</sub> (Volatec Oy), and the Co precursor, cobalt acetyl acetonate, Co(acac)<sub>3</sub> (Merck, 98%), were fed to the support with nitrogen as a carrier gas at 180 °C for 6 h at reduced pressure. An excess amount of precursor was used. Thereafter, the unreacted precursor was flushed from the reactor with nitrogen. The reaction cycles were alternated and repeated to achieve the desired metal loading. The abbreviations

for the catalysts used in this paper represent the number and order of different precursor cycles, for example the Pt catalyst is a catalyst prepared using one Pt precursor cycle and the PtCo catalyst is prepared using one Pt precursor cycle followed by one Co precursor cycle. To obtain catalysts with different metal depositions, catalysts with varying precursor cycles were prepared sequentially by taking part of the initial catalyst from the reactor and adding metal cycles to the remaining part of it. To ensure the homogeneity of the catalyst, the batch sizes of the prepared catalyst were kept rather small; because of the amount of catalyst material needed for different characterizations, the prepared catalyst for all of the batches were not characterized after every cycle.

### 2.2. Physical characterization

The metal loadings on the ALD-prepared catalysts were determined by atomic emission spectroscopy (AES) (ICP-AES, Varian Liberty series II).

All of the studied catalysts were characterized by X-ray diffraction (XRD) (PanAnalytical X'Pert Pro). The XRD diffractograms were used to calculate the size of crystalline domains using the Scherrer equation (Eq. 1):

$$d = \frac{0.9\lambda}{\beta_{2\theta} \cos \theta}, \quad (1)$$

where  $d$  is the average crystalline domain diameter in nm,  $\lambda$  is the X-ray wavelength (Cu target 1.540 nm),  $\theta$  is the Bragg angle in radians, and  $\beta_{2\theta}$  is the full width at half maximum (FWHM) in radians. Crystalline domains are assumed to be monocrystals and the crystalline domain size  $d$  is discussed as the metal particle size in the article.

High-resolution transmission electron microscopy (HRTEM) was performed using a double-aberration-corrected JEOL 2200FS (JEOL) microscope equipped with a field emission gun (FEG) operating at 200 kV. The TEM was equipped with an energy dispersive X-ray (EDX) spectrometer for elemental analysis. A Gatan 4k × 4k UltraScan 4000 CCD camera was employed for digitally recording the HRTEM images. Gatan Digitalmicrograph software was used for camera control and image processing. The metal particle size was measured using the TEM images and the average metal particle sizes were calculated as arithmetic averages based on the measurements from the TEM images, assuming that those particles are of a spherical shape.

X-ray photoelectron spectroscopy (XPS) (SSX-100) was performed to measure the atomic surface concentration of metals and to analyze the metal oxidation states. The experiments were carried out using monochromatic AlK $\alpha$  X-rays and an electrostatic hemispherical analyzer. The spectra were recorded with a pass energy of 160 eV, a measurement area of 1 mm in diameter, and a spot size of 0.05 eV. A high pass energy and large spot size were chosen to maximize the intensity level. For calculation of the surface concentrations, the platinum 4f, cobalt 2p, carbon 1s and oxygen 1s peaks were considered. The atomic concentrations obtained from XPS were converted into mass percentages for comparison with other methods. All of the binding energies were referenced to the carbon 1s peak at 284.5 eV.

CO chemisorption (Omnisorp 100CX) was performed to measure the active surface area of the catalysts as well as the particle size. In these standard procedure experiments, the catalysts were reduced 350 °C with hydrogen as a pretreatment before the CO chemisorption was performed at 30 °C. In the reduction, pure hydrogen (AGA, 99.999%) was fed through the sample and the pressure increased close to atmospheric pressure because of the flow. Before the CO chemisorption, the pressure was decreased to the vacuum and pulses of CO were fed. During the CO pulses, the pressure increased and the pressure increase was measured.

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