

METHANOL OXIDATION CATALYST BY ATOMIC LAYER DEPOSITION

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Abstract

Direct liquid fuel cells (DMFCs) are very appealing alternatives for fighting climate change, particularly in the field of personal mobility solutions. However, DMFCs also have some serious competitive disadvantages, like the high cost of the noble metal catalysts, the difficulties of the catalyst application, and the poisoning of the catalyst due to carbon monoxide formation. Here we demonstrate that depositing platinum on TiO₂ by atomic layer deposition (ALD) is an easy, reproducible method for the synthesis of TiO₂-supported platinum catalyst for methanol oxidation with excellent anti CO poisoning properties.

Introduction

Direct liquid fuel cells (DMFCs) enjoy increasing scientific attention today due to their low working temperature, high power density, and compact size. The most universally used catalysts in DLFCs today are platinum and platinum group metals. Despite of its drawbacks, platinum shows excellent electrocatalytic properties in most fuel cells. It is the most used catalyst for both the cathodic side as oxygen reduction reaction (ORR) and the anodic side as hydrogen oxidation reaction (HOR) or methanol oxidation reaction (MOR) catalyst. However, during the last process, carbon monoxide forms as an intermediate that can have serious negative effects on the performance of the catalyst due to the strong CO-Pt interactions. Transition metal oxides, including titanium oxides, are widely used as catalyst support materials due to their high surface area and excellent chemical stability. In MOR metal oxides also help the oxidation of carbon monoxide and reduce anode catalyst poisoning. One of the main setbacks of the oxides is their low electrical conductivity, especially compared to the other supporting materials used in fuel cells, such as carbon structures or metal foams [1],[2],[3],[4]

Experimental

Working electrodes were synthesised by atomic layer deposition, depositing a titanium dioxide layer and platinum nanoparticles on AvCarb P75 carbon paper support. The Beneq TFS 200 ALD equipment was used during the process. To prepare the electrode, first 25 cycles of TiO₂, then 20 cycles of platinum were deposited on the same GDL (25c TiO₂ & 20c Pt). For comparison, we also prepared carbon paper/Pt nanoparticle electrodes without the underlying titanium dioxide layer (20c Pt). Before and after the synthesis the weight of the carbon paper was measured to calculate the weight of the deposited materials. The TiO₂ loading was 0.019 mg cm⁻², while the platinum loadings were 0.277 and 0.116 mg cm⁻² in 20c Pt and 20c Pt & 25c TiO₂ catalysts, respectively.

The as-synthesized catalysts were characterized by transmission electron microscopy. A FEI Tecnai G2 20 X-Twin microscope was used. The crystal structure of the electrodes was analyzed by powder X-ray diffraction measurements (XRD). The Cu K α radiation was generated by a Philips PW1830 X-ray generator operating at 40 kV.

The electrochemical measurements were conducted in a custom made three-electrode PTFE cell using an ACM Instruments Gill AC potentiostat at room temperature. ALD modified AvCarb P75 carbon papers were used as working electrodes, while Ag/AgCl (3 M NaCl) and Pt wire were utilized as reference and counter electrodes, respectively. The two halves of the cell were separated by a glass frit. During the measurements 0.5 M sulphuric acid and 0.5 M sulphuric acid + 0.5 M methanol were used as electrolytes. The electrochemical properties of the ALD modified electrodes were examined by cyclic voltammetry between 0 and 1200 mV vs RHE at a sweep rate of 10 mV s⁻¹. The electrochemical surface area (ECSA) of the catalysts was calculated from the hydrogen adsorption/desorption region of the obtained voltammograms by the following equation:

$$ECSA (m^2 g_{Pt}^{-1}) = \frac{Qh (mC cm^{-2})}{0.21(mC cm^{-2}) * W_{Pt}(mg_{Pt} cm^{-2})} * 10^{-1}$$

Here, Qh is the charge calculated from the H_{des} region of the voltammogram, while the 0.21 represents a charge required to oxidize a monolayer of hydrogen adsorbed on Pt and the W_{Pt} is the loading of platinum [5],[6]. The methanol oxidising properties and the CO tolerance of the electrode were evaluated from the CV measured in the methanol containing electrolyte by comparing the ratio of the peak current during the forward (i_f) and the backward (i_b) scan. It is generally accepted that the ratio of these peaks is correlated with the tolerance of the catalyst to carbonaceous species. An increase in the i_f/i_b ratio means enhanced CO oxidation properties of the catalyst [7].

Results and discussion

As can be seen in Fig 1.(a,b) platinum nanoparticles are well distributed on the surface of the carbon support, while only fewer nanoparticles formed in the titanium dioxide containing gas diffusion electrode. The average particle sizes were 3.2 nm, and 2.4 nm in 20c Pt and 25c TiO₂ & 20c Pt catalysts, respectively. The difference in particle size could be attributed to the difference of the surface energy, and consequently, the wettability of the carbon and TiO₂ covered carbon supports. The smaller particle size implies higher surface area, which in turn means more active sites for methanol oxidation.

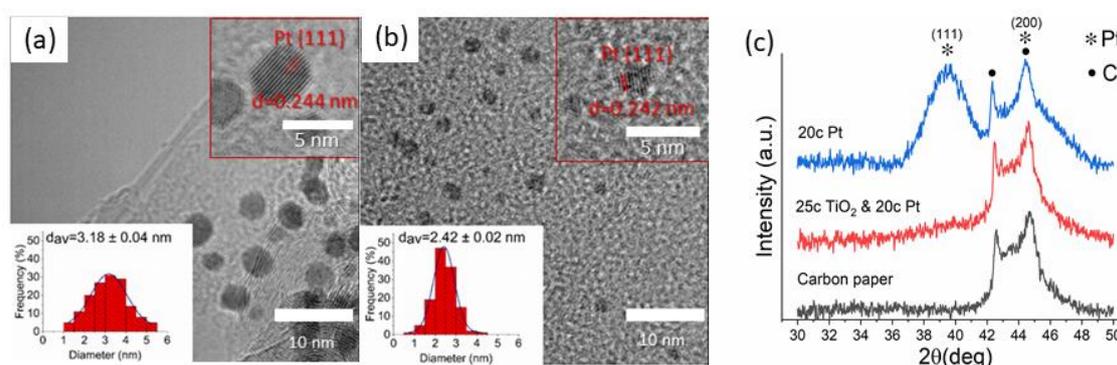


Figure 1.: TEM images(a,b) and the characteristic XRD patterns of the ALD synthesised 20c Pt and 25c TiO₂ & 20c Pt catalysts

Fig 1.(c) shows the XRD patterns of the ALD-synthesised electrodes. In the case of 20c Pt electrode, the two reflections at 39.5° and 44.4° correspond to the platinum (111) and (200) planes. In the case of the titanate containing electrode, the reflections of platinum are broadened

because of the smaller particle size. In bare carbon paper, the two reflections are attributed to the (100) and (101) planes of the graphite content of the carbon fibre GDL.

The electrocatalytic properties of the ALD-synthesised electrodes were investigated by cyclic voltammetry (CV). The hydrogen adsorption/desorption region is visible between 0 and 0.4 V (vs. RHE) in Fig 2. (a).

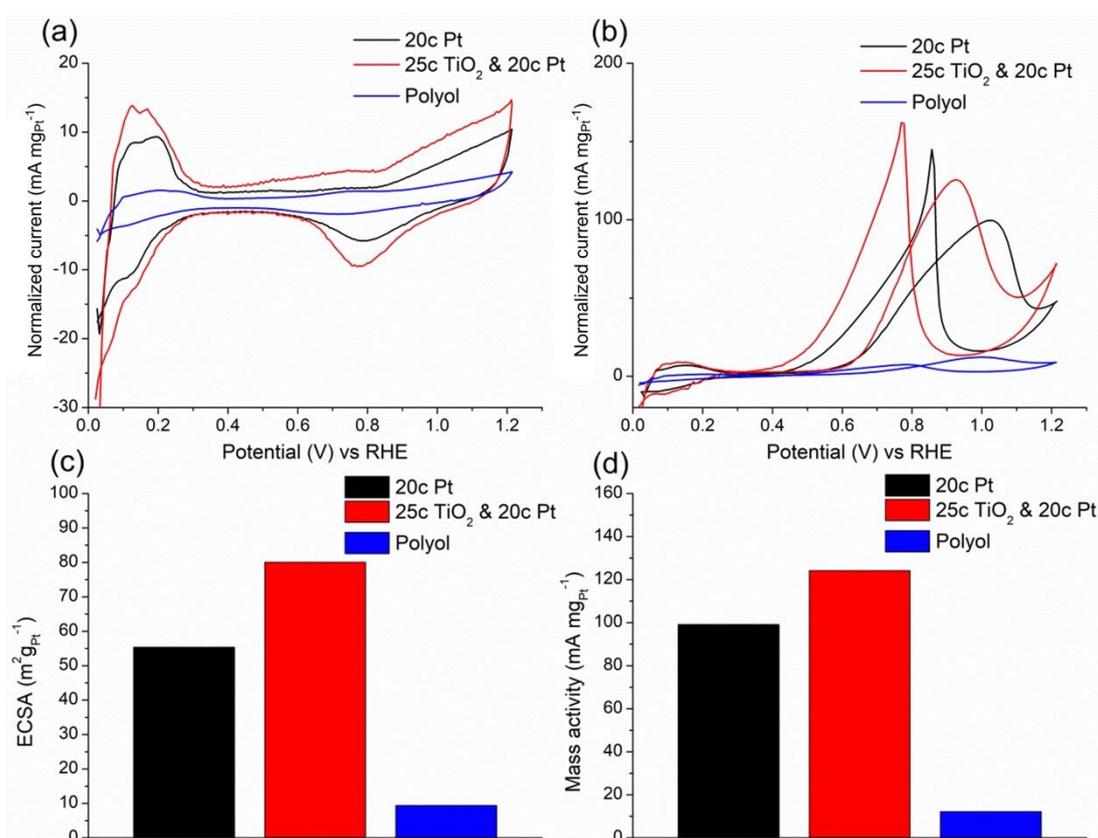


Figure 2.: The cyclic voltammograms measured in 0.5 M H₂SO₄ (a) and 0.5 M methanol / 0.5 M H₂SO₄ electrolytes (b), the electrochemically active surface area (c) and the mass activity (d) of the ALD synthesised catalysts compared to the drop-casted platinum nanoparticle catalysts

The electrochemical surface area was calculated as 55.35 and 80.05 m² g_{Pt}⁻¹ for the 20c Pt and 25c TiO₂ + 20c Pt catalysts, respectively. The methanol oxidation properties of the electrodes were evaluated by measuring cyclic voltammograms in 0.5 M sulphuric acid/0.5 M methanol electrolyte. The higher the i_f/i_b ratio (i.e., the ratio of the peak current of the forward (i_f) and backward (i_b) scan), the more efficient the oxidation of methanol to CO₂, which means less carbonaceous species accumulation on the surface of the catalyst [8].

Conclusion

Atomic layer deposition is a suitable method to synthesize well-distributed platinum nanoparticles on carbon paper and titanate covered carbon paper supports, where both the platinum and TiO₂ were synthesised by ALD. The morphology and the crystal structure of the as-prepared electrodes were characterised and the electrocatalytic methanol oxidation activity was evaluated. This yielded platinum nanoparticles with high electrochemical surface area and mass activity with the use of titanate covered carbon paper GDL support. The mass activity of the new catalyst exceeded that of the reference Pt catalyst obtained by traditional wet chemistry

by one order of magnitude. Moreover, the increased i_f/i_b ratio leads to better methanol oxidation properties and renders the reported preparation method a promising alternative for creating poisoning tolerant anode catalysts in DMFCs.

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