Accurate tuning of ordered nanotubular platinum electrodes by galvanic plating†

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Platinum nanotubes are created by galvanic deposition inside porous templates. The effects of the electrolyte’s ion concentration and pH, of the applied potential and of the deposition duration on the morphology of the tubes are investigated systematically. The system provides a model electrode platform with accurately tunable geometry for the fundamental investigation of electrochemical transformations. For slow electrochemical reactions, we observe a linear increase of the galvanic current with the length of the nanotubes, and therefore with the specific surface area of the electrode. In contrast to this, inherently fast electrochemical transformations are diffusion-limited and give rise to the same current density independently of the geometry. These results delineate a strategy for optimizing the performance of electrochemical energy conversion devices systematically via nanostructuring the electrode surfaces.

Introduction

Nanostructured electrode surfaces are broadly considered as a promising strategy towards efficient, cost-effective energy-converting or energy-storing devices such as batteries, fuel cells, electrolyzers, and solar cells. Energy conversion relies on the transfer of electrons across an interface, so that the enhanced specific surface area of a structured electrode could allow for an increased throughput. Simultaneously, the transport of charge carriers (electrons and holes, but also ions and molecules) towards the interface and back away from it may become limiting. Therefore, device performance improvements by electrode nanostructuring must result from an optimized geometry which balances interface area gain with short transport paths.

Despite impressive individual achievements, a general knowledge of the scientific parameters underpinning these phenomena (interfacial electron transfer rates, reaction mechanisms, and diffusion constants) is still missing.

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the galvanic current as a function of the nanotube length for various reactions with contrasting electrode kinetics.

**Preparation**

The preparation combines two major ingredients. Firstly, we use a template that provides the overall order of the tubes and defines their diameter. Secondly, we perform the galvanic plating of platinum under conditions such that it results in the coating of the pore walls and thereby the formation of tubes instead of the complete filling of the pore volume, which yields solid wires. The inner surface of the platinum nanotubes later serves as the electrochemically active area. The electrochemical deposition of tubes instead of wires in elongated pores can be controlled by the formation of a dihydrogen bubble at the lower pore extremity. In this case, the morphology and wall thickness depend on the concentration of metal ions, pH, and applied potential in a predictable manner.

In the first step, these effects were studied with polycarbonate 'track-etch' filters serving as templates with 200 nm pore diameter, after an electrical contact was defined on one side by sputter-coating of a thin gold layer, followed by a short galvanic deposition of gold from a commercial electrolyte. Hexachloroplatinic acid (6.0 mM) was used in 1.0 M sulfuric acid as an electrolyte. Under these conditions, the application of a potential of +0.40 V or lower yields solid wires. The inner surface of the platinum nanotubes later serves as the electrochemically active area. The electrochemical deposition of tubes instead of wires in elongated pores can be controlled by the formation of a dihydrogen bubble at the lower pore extremity. In this case, the morphology and wall thickness depend on the concentration of metal ions, pH, and applied potential in a predictable manner.

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Alternatively, the morphology of the deposit can be affected by the pH. Within the range $0 \leq \text{pH} \leq 2.4$ accessible by adding sulfuric acid to the 2.0 mM chloroplatinic acid electrolyte, we find significant variation of neither the galvanic current density nor the tube wall thickness upon pH at either $-0.8$ V, $-0.4$ V or 0 V. However, when potassium hydrogen phosphate (0.12 M) is acidified with hydrochloric acid, a clear trend emerges at all three applied potentials, documented in Fig. 3, which once again qualitatively follows the model put forth previously.10

The model, however, does not account for the wall thickness variation observed when tubes obtained after various deposition times are compared with each other. Fig. 4 documents that tubes grown at very negative potentials tend to thin out whereas those grown closer to equilibrium conditions will close down to wires.

The method established in the track-etch membranes can be transferred to another, more ordered, class of porous templates, namely, porous ‘anodic’ alumina. The anodization of aluminum at $+195$ V in phosphoric acid results in the creation of hexagonally ordered cylindrical pores,13,14 in which Pt wires and tubes can be grown under the conditions described above. Fig. 5 shows ordered arrays of Pt nanowires obtained in this type of template. We note that beyond a length of approximately 2 μm, the wall thickness is no longer constant, in agreement with the observations presented in Fig. 4. Pores of 10 μm or more can only be filled with either solid wires or thin-walled tubes.

The chemical identity of the deposit is established by energy-dispersive X-ray spectroscopy and X-ray diffraction. The X-ray diffractogram (Fig. 6) displays the peaks expected of fcc Pt,15–17 in addition to those of the underlying Au contact. The amorphous alumina matrix contributes a very broad background signal.
Electrode behavior

The structured material deposited here displays the electrochemical behavior expected for platinum. The cyclic voltammogram recorded in 1 M H₂SO₄ when an array of nanotubes is used as the working electrode (black curve in Fig. 7) is in perfect agreement with the literature precedents reported for flat platinum electrodes. The two reversible peaks at negative potential are due to the reductive uptake of hydrogen adatoms from the electrolyte and their oxidative loss. The poorly reversible wave near +0.5 V corresponds to the oxidative formation of surface hydroxides and oxides and their reductive loss. Finally, oxygen evolution sets on beyond +1.2 V. More interestingly, such Pt nanotube arrays can also provide a platform for the electrochemical oxidation of ethanol, found in direct ethanol fuel cells. The essentially perfect match obtained between our electrochemical curves (Fig. 7, red) and those published for flat reference samples furnishes an additional example for the electrochemical competence of our nanotubular system. In line with Goodenough’s report, the nanostructured electrode gives rise to the cathodic peak labeled Rb in the absence of alcohol only (reduction of adsorbed Pt–OH moieties), whereas in its presence, one observes the anodic waves O1’ and O2’ (attributed to the oxidation of adsorbed formyls and carbonyls to CO₂, respectively) on the anodic scan, as well as an additional, unusual anodic feature O³ on the cathodic sweep (due to the three-electron oxidation of adsorbed Pt–CO groups upon one-electron reduction of Pt–OH).

This electrode system now provides a well-defined and broadly tunable platform for the investigation of transport effects in electrochemical reactions: by varying the platinum tube length, the experimenter can change the electrode’s specific surface area in direct proportion to the length of the ion diffusion paths in the solution towards the solid surface. For this purpose, electrodes can be prepared from anodic alumina membranes of various thicknesses, in which Pt nanotubes are grown until they reach the pore extremity and a continuous Pt layer develops atop the membrane. This solid metallic layer is then utilized as the electrical contact for the subsequent electrochemical measurements: the sample is flipped over and Au removed in a KI₃ solution. When electrodes prepared in this way with 10 µm to 30 µm long Pt tubes (200 nm diameter, 20(±10) nm wall thickness) are poised at +0.20 V in an aqueous solution of 0.05 M potassium hexacyanoferrate(Ⅲ), the galvanic current stabilizes at similar values for all of them (Fig. 8). This is in line with the well-established fast one-electron transfer reactions of the [Fe(CN)₆]³⁻/⁴⁻ redox couple. In this case, ion transport from the bulk solution to the interface is slower than electron transfer at the interface, so that the increase of interface area leads to no significant gain in galvanic throughput. The situation is different for slow multielectron transformations such as the two-electron reduction of water. Here (at ~0.30 V in 0.5 M H₂SO₄), the current increases with the tube length in a linear manner (Fig. 8). In this case, the diffusion of protons is fast with respect to their reduction to dihydrogen at the surface. Therefore, the full surface area of the tubes participates in the electrochemistry no matter how deeply buried some of the electrodes may be. The oxidation of ethanol, a reaction of interest for fuel cells, behaves in a similar manner. This is also

![Image](Image 14x290 to 26x354)

Fig. 7  Cyclic voltammetric traces recorded at a nanotubular Pt electrode in aqueous H₂SO₄ solution (0.5 M, black) and after addition of ethanol (0.5 M, red). The curves are offset for clarity. The measurements were initiated at −0.20 V (vs. Ag/AgCl/KCl(sat.) reference) in the anodic direction at 100 mV s⁻¹. The measurements in ethanol solution evolved with repeated cycling: the first ten cycles are displayed in increasingly light color.

![Image](Image 309x178 to 546x349)

Fig. 8  Steady-state electrochemical current densities j recorded for three distinct reactions at electrodes made out of Pt nanotubes with various lengths L. Experimental conditions: black, 0.05 M K₄Fe(CN)₆, +0.2 V; red, 0.5 M H₂SO₄, −0.30 V; green, 0.5 M H₂SO₄, 0.5 M ethanol, +1.1 V (all potentials are reported with respect to Ag/AgCl). The current can vary by up to 20% over time (vertical error bars). The linear fits shown as dashed lines highlight the contrasting behavior of these reactions: the current density increases linearly with the electrode’s specific surface area in the case of slow electrochemical transformations (water reduction and ethanol oxidation), whereas it is independent of it for the fast oxidation of hexacyanoferrate(Ⅲ), which is diffusion-controlled.

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a slow, multielectron transformation which profits from an increased specific surface area despite the longer diffusion pathways associated with the nanopores, as is apparent in Fig. 8 (data taken in acidic ethanol solution at +1.1 V).

Conclusions

Taken together, our results establish the applicability of a nanotubular platinum/alumina system as a model with well-defined, tunable geometry for systematic investigations of electrochemical reactions. The system is prepared exclusively using simple electrochemical techniques. The electrode consists of the electrochemist’s standard material platinum, but the system can be generalized to other metal compositions with tailored catalytic activity. The length of the tubes is defined by the duration of the galvanic plating procedure and/or by the thickness of the porous template, their diameter by the conditions of the aluminum anodization, and their wall thickness by the parameters of the galvanic plating. The influence of pH, hexachloroplatinate concentration and applied potential on the morphology of the deposit obtained after short deposition times are all in qualitative agreement with a published theoretical model. The limitations of the theory become apparent for longer deposition durations, where the tube wall thicknesses evolve with time.

At nanotubular surfaces obtained with these methods, the electrolytic current associated with some difficult and inherently slow multielectron reactions depends on the specific surface area linearly. These results are directly applicable to various types of electrochemical devices, in particular batteries and fuel cells, in which electrodes can now be structured in a systematic manner.

Materials and methods

All solutions were prepared with water from a Millipore DirectQ system. Chemicals were purchased from VWR, Sigma Aldrich or Strem Chemicals and used without further purification. Nucleopore track-etch polycarbonate membrane filters were purchased from Whatman with a nominal pore diameter of 200 nm and thickness of 5 µm. A 70 nm thick Au layer was deposited onto one side of the membrane as an electrical contact with a Cressington sputter coater 108. Subsequently, a thicker gold layer was obtained from an Auruna 5000 electroplated onto one side of the membrane as an electrical contact by the parameters of the galvanic plating. The influence of pH, hexachloroplatinate concentration and applied potential on the morphology of the deposit obtained after short deposition times are all in qualitative agreement with a published theoretical model. The limitations of the theory become apparent for longer deposition durations, where the tube wall thicknesses evolve with time.

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Ordered arrays of cylindrical platinum nanotubes are generated by galvanic methods. They serve as model structured electrode surfaces with well-defined geometry. Systematically increasing the tube length results in linear increases of the electrochemical current density for slow, surface-limited reactions.

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