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PRINCIPAL INVESTIGATOR: Mark Hersam

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14. ABSTRACT Iridium oxide (IrOx) has been widely studied due to its applications in electrochromic devices, pH sensing, and neural stimulation. Previous work has demonstrated that both Ir and IrOx films with porous morphologies prepared by sputtering exhibit significantly enhanced charge storage capacities. However, sputtering provides only limited control over film porosity. In this work, we demonstrate an alternative scheme for synthesizing nanoporous Ir and activated IrOx films (AIROFs). This scheme utilizes atomic layer deposition to deposit a thin conformal Ir film					
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Synthesis of nanoporous activated iridium oxide films by anodized aluminum oxide templated atomic layer deposition

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Synthesis of nanoporous activated iridium oxide films by anodized aluminum oxide templated atomic layer deposition

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Iridium oxide (IrOx) has been widely studied due to its applications in electrochromic devices, pH sensing, and neural stimulation. Previous work has demonstrated that both Ir and IrOx films with porous morphologies prepared by sputtering exhibit significantly enhanced charge storage capacities. However, sputtering provides only limited control over film porosity. In this work, we demonstrate an alternative scheme for synthesizing nanoporous Ir and activated IrOx films (AIROFs). This scheme utilizes atomic layer deposition to deposit a thin conformal Ir film within a nanoporous anodized aluminum oxide template. The Ir film is then activated by potential cycling in 0.1 M H₂SO₄ to form a nanoporous AIROF. The morphologies and electrochemical properties of the films are characterized by scanning electron microscopy and cyclic voltammetry, respectively. The resulting nanoporous AIROFs exhibit a nanoporous morphology and enhanced cathodal charge storage capacities as large as 311 mC/cm².

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1. Introduction

Iridium oxide (IrOx) has been studied and utilized for a wide range of applications including electrochromic devices [1,2], pH sensing [3,4], and neural stimulation [5,6]. IrOx is particularly well-suited for neural stimulation due to the large charge storage capacities associated with faradaic reactions between Ir³⁺ and Ir⁴⁺ redox states within the oxide [7]. Furthermore, IrOx is both biocompatible and corrosion resistant, which are additional requirements for neural stimulation electrodes.

IrOx synthesis has been demonstrated by a number of strategies. Among the most common is the formation of activated IrOx films (AIROFs) by repeated potential cycling or pulsing of Ir metal in acid or phosphate-buffered electrolytes [8,9]. IrOx films have also been synthesized by a number of deposition strategies, including sputtering [10–12] and electrodeposition [13,14]. With all synthesis strategies, control of the film morphology is particularly important, as increased film porosity has been found to enhance charge storage capacity in both AIROFs [15] and sputtered IrOx films [12].

In this work, we demonstrate an alternative scheme for synthesizing morphologically controlled Ir films that enables nanoporous AIROFs with enhanced charge storage capacity. This approach utilizes atomic

layer deposition (ALD) of a thin conformal Ir film into a nanoporous anodized aluminum oxide (AAO) template. AAO templates consist of hexagonally-ordered pores with controlled pore spacings and diameters [16,17] and have been widely used to prepare nanoporous materials [18,19]. ALD is a deposition technique utilizing iterative, self-limiting surface reactions to deposit thin films in a monolayer-by-monolayer fashion [20] that enables films with precise thickness and compositional control, high conformality, and uniform infiltration of porous templates [21–24]. Detailed synthetic procedures and thorough experimental characterization are presented below, thus establishing the advantages of nanoporous AIROFs for charge storage and pH sensing applications.

2. Experimental details

2.1. Anodized aluminum oxide template synthesis

AAO templates consisting of 350 nm diameter, 18 μm long pores with 425 nm spacing were prepared using a two-step anodization procedure [16]. Anodizations were conducted at 170 V in 0.3 M H₃PO₄ at 5 °C and exhibited a growth rate of 0.3 μm/min. Following anodization, pores were widened by etching in 10 wt.% H₃PO₄ at 35 °C for 1 h.

2.2. Atomic layer deposition of Ir metal

Flat and nanoporous Ir films were prepared by ALD onto glass and AAO templates, respectively. Ir ALD was conducted in a viscous flow

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reactor [25] maintained at a pressure of ~ 1 Torr under a flow of 130 sccm N_2 (99.999% purity) carrier gas and a temperature of $300^\circ C$. After loading into the reactor, all substrates were thermally equilibrated for 10 min and then cleaned *in situ* by exposure to 10% ozone in 400 sccm O_2 for 10 min. A $20\text{ \AA}$ Al_2O_3 film was then deposited as a nucleation layer by iterative exposures of trimethylaluminum and H_2O [26]. Ir films were then deposited by iterative exposures of iridium(III) acetylacetonate ($Ir(acac)_3$), maintained within a stainless steel bubbler at $170^\circ C$, and O_2 . [26] Ir ALD was conducted with 5–10 s $Ir(acac)_3$ exposures and 2 s O_2 exposures, with

each exposure followed by a 5 s N_2 purge. All Ir films were deposited for 600 cycles and were ~ 27 nm thick.

2.3. Electrochemical activation and characterization

Both flat and nanoporous Ir films were electrochemically activated to form AIROFs. For all electrochemical measurements, electrical contact was made to the films with Ag paint and the films were masked with a chemically-resistant vinyl masking tape to define a $0.125''$ diameter electrode. The AIROFs were prepared by 200 cycles of

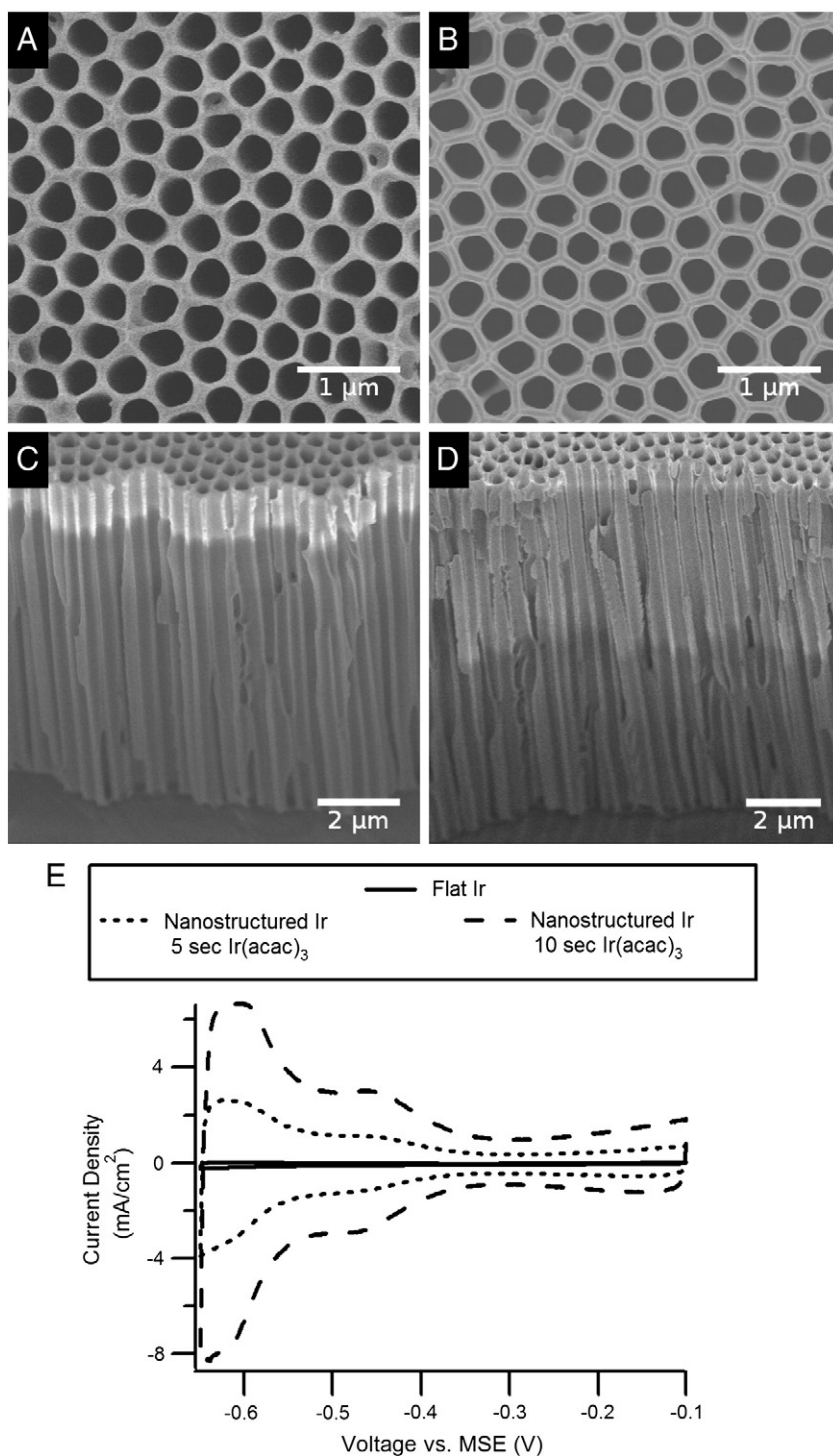


Fig. 1. SEM images of the top surface of the AAO template A) before Ir ALD and B) after 600 cycles of Ir ALD. Cross-sectional SEM images of AAO templates with a 600 cycle Ir ALD film deposited with C) 5 s $Ir(acac)_3$ exposures and D) 10 s $Ir(acac)_3$ exposures. E) CV in 1 M H_2SO_4 of flat and nanoporous Ir films demonstrating the surface area enhancement of the nanoporous films.

potential cycling in 0.1 M H₂SO₄ between −0.7 and 0.8 V vs. mercury/mercurous sulfate electrode (MSE) at a scan rate of 100 mV/s [27]. Immediately following activation, the AIROFs were characterized by cyclic voltammetry (CV) in 1 M H₂SO₄ between −0.7 and 0.8 V vs. MSE at a scan rate of 100 mV/s. The cathodal charge storage capacity (CSC_c), which provides a measure of the total charge stored within the IrOx film and available for a stimulation pulse, was determined by CV between −0.6 and 0.8 V vs. Ag/AgCl in a phosphate-buffered saline solution (22 mM NaH₂PO₄, 81 mM Na₂HPO₄, and 130 mM NaCl). The CSC_c was calculated as the time integral of the negative current over a complete CV cycle [28].

Potentiometric pH sensing with the AIROFs was assessed by measuring the open circuit voltage vs. saturated calomel electrode (SCE) in commercial buffer solutions ranging in pH from 2 to 10. Samples for pH testing were activated for 200 cycles with the final activation cycle ending at 0.8 V. The sample was then immersed in H₂O for at least 12 h prior to pH testing.

3. Results and discussion

3.1. Morphology of nanoporous Ir metal films

The nanoporous Ir metal films prepared by ALD into AAO templates are shown in Fig. 1. As is characteristic of ALD films, the Ir film conformally coats both the top and internal surfaces of the nanoporous template. Additionally, cross-sectional images demonstrate that the infiltration depth of Ir within the template is controlled by the Ir(acac)₃ exposure time, with 5 and 10 s exposure times resulting in infiltration depths of 2.2 and 9 μm, respectively. As shown in Fig. 1E, the nanoporous Ir films exhibit enhanced faradaic currents associated with hydrogen adsorption/desorption relative to flat Ir films. These enhanced currents confirm the enhanced surface area of the nanoporous Ir film and its suitability for subsequent activation.

3.2. Characterization of AIROFs

Nanoporous AIROFs are prepared by potential cycling in 0.1 M H₂SO₄. As shown in Fig. 2A, there is significant volume expansion associated with the conversion of Ir to IrOx during activation. While such volume expansion occurs with all AIROF schemes, this nanoporous AIROF synthesis scheme is advantageous in that the volume expansion can be accommodated by appropriately selecting the template dimensions. In comparison, other strategies for depositing Ir films with enhanced porosity, such as sputtering, are

only capable of small-scale porosity with pores on the order of 20 nm [15]. Based upon the observed volume expansion, such small-scale porosity will be completely eliminated upon conversion to IrOx. This behavior was confirmed in our lab, with a 90 nm diameter nanoporous Ir film exhibiting near complete pore occlusion after 100 activation cycles. However, by appropriately selecting large diameter porous templates, as in this work, thicker Ir films and more extensively activated IrOx films can be achieved while retaining the porosity necessary to maintain electrolyte access to the large internal surface area of the nanoporous AIROF.

The AIROFs are also characterized by CV in 1 M H₂SO₄. As shown in Fig. 2B, both flat and nanoporous AIROFs exhibit peaks at 0.34 and 0.155 V due to faradaic reactions between the Ir³⁺ and Ir⁴⁺ redox states within the IrOx film, thus confirming the formation of IrOx during activation. The enhanced currents exhibited by the nanoporous AIROFs are due to the increased infiltration of the nanoporous template and increased volume of IrOx formed during activation.

Additionally, as shown in Fig. 2C, the nanoporous AIROFs exhibit enhanced CSC_c, with the 5 and 10 s Ir(acac)₃ nanoporous AIROFs exhibiting 127 and 311 mC/cm², respectively, and the flat AIROF exhibiting 18.7 mC/cm². The large CSC_c of nanoporous AIROFs is highly desirable, as more charge can be delivered per stimulation pulse. However, the magnitude of the CSC_c is also significant with regards to mechanical stability. With more conventional AIROFs formed on Ir thin films or foils, large CSC_c values are commonly achieved by forming thicker IrOx films. However, these thicker IrOx films are more likely to exhibit delamination or other mechanical failures, especially at CSC_c > 80 mC/cm². However, the nanoporous AIROFs are less susceptible to these problems, as the primary factor determining CSC_c is the infiltration depth of the Ir ALD film rather than the thickness of the IrOx film. As a result, the nanoporous morphology enables a large CSC_c to be achieved with relatively thin IrOx films that do not suffer from delamination. This mechanical robustness was confirmed by the nanoporous AIROFs exhibiting no reduction in CSC_c after being subjected to ultrasonication treatments. The ability to achieve large CSC_c with thin IrOx films also has significant practical advantages, in that fewer activation cycles are required, which allows for quicker fabrication of such films.

3.3. pH sensing with AIROFs

Both flat and nanoporous AIROFs exhibit similar pH responses, with the flat AIROF exhibiting a slope of 69.2 mV/pH and the nanoporous AIROF exhibiting 67.5 mV/pH. The similar pH responses demonstrate

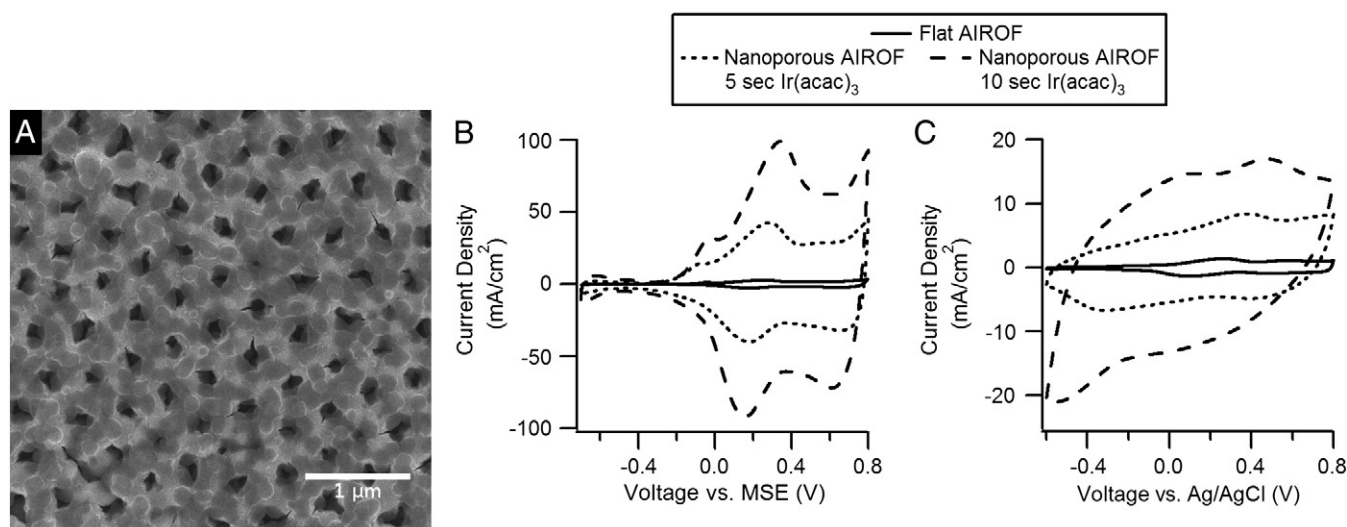


Fig. 2. A) SEM image of the top surface of the AAO template following 200 cycles of activation in 0.1 M H₂SO₄. B) CV scans in 1 M H₂SO₄ of flat and nanoporous AIROFs. C) CV scans in phosphate-buffered saline of flat and nanoporous AIROFs demonstrating the enhancement in CSC_c.

that the nanoporous morphology does not significantly affect the film characteristics. Furthermore, the slope of the pH response provides information regarding the hydration of the IrOx film. As anhydrous IrO₂ is characterized by a Nernstian response with a slope of ~59 mV/pH [29], the super-Nernstian response indicates that the AIROFs are at least partially hydrous in nature [29,30], which is consistent with AIROF synthesis [31].

4. Conclusions

The application of ALD to AAO templates allows for the synthesis of nanoporous Ir films and AIROFs, and provides a number of advantages over alternative synthesis strategies. ALD enables precise control over the Ir film thickness and infiltration depth, while AAO provides a well-defined, tunable nanoporous template. The precise control over film morphology is especially important considering the significant volume expansion observed upon IrOx formation. By utilizing appropriate ALD templates, AIROFs retaining a highly nanoporous morphology can be synthesized. This nanoporous morphology yields significantly enhanced CSC_c values of 311 mC/cm² for nanoporous AIROFs compared to only 18.7 mC/cm² for flat AIROFs, while also maintaining the mechanical stability of thinner IrOx films. Additionally, both flat and nanoporous AIROFs exhibit similar pH responses, which demonstrate the potential for these films in pH sensing applications. Lastly, due to the precise control and tunability of the nanoporous AIROF film morphology enabled by AAO templates and ALD, future work will focus on investigating the effects of AIROF porosity in neural stimulation applications and on determining optimal porosities and film structures for such applications.

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