An improved molecular-level description of trans-membrane ion currents has the potential to impact many areas of military and civilian importance such as disease diagnosis, drug development/screening, and technologies that interface between living cells and microelectronic circuitry. Ultimately, these developments would imply improvements in health and quality of life for individuals that have suffered from injuries or wounds that have compromised senses such as sight and hearing. Furthermore, technologies involving the human-machine interface.
ABSTRACT

An improved molecular-level description of trans-membrane ion currents has the potential to impact many areas of military and civilian importance such as disease diagnosis, drug development/screening, and technologies that interface between living cells and microelectronic circuitry. Ultimately, these developments would imply improvements in health and quality of life for individuals that have suffered from injuries or wounds that have compromised senses such as sight and hearing. Furthermore, technologies involving the human-machine interface and disease diagnosis/treatment are likely to be positively impacted. This AROYIP/PECASE, entitled "Nanoscale Probing of Electrical Signals in Biological Systems," is developing conductive atomic force microscopy (AFM) techniques, such as scanning electrochemical microscopy (SECM) and scanning ion conductance microscopy (SICM), with the potential to improve the spatial resolution of trans-membrane ion channel measurements by at least an order of magnitude over the current state-of-the art. In addition, nanostructured biocompatible neural stimulation electrodes are being fabricated and characterized. Beyond trans-membrane ion channels, advanced SECM and SICM methods have also been applied to other materials systems including electrochemically active electrodes, nanocomposites, graphene, and photovoltaics.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)
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M. J. Schmitz, C. R. Kinser, N. E. Cortes, and M. C. Hersam. Ambient atomic force microscope nanoscale oxidation of hydrogen-passivated silicon with conductive diamond coated probes, Wiley InterScience, (03 2007): . doi:

N. E. Sosa, J. Liu, C. Chen, T. J. Marks, and M. C. Hersam. Nanoscale writing of transparent conducting oxide features with a focused ion beam, Advanced Materials, (02 2009): . doi:

TOTAL: 18

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations


M. C. Hersam, “Chemically refined carbon nanoelectronic materials,” presented orally by M. C. Hersam at the AVS Prairie Chapter Symposium, Evanston, Illinois (9/1/11).

M. C. Hersam, “Molecular-scale tailoring of graphene surface chemistry via organic functionalization,” presented orally by M. C. Hersam at the NT11 Graphene Technology Satellite Workshop, Cambridge, United Kingdom (7/15/11).

M. C. Hersam, “Probing photon-matter and electron-matter interactions at the molecular scale,” presented orally by M. C. Hersam at the 7th Annual Meeting on Condensed Phase and Interfacial Molecular Science, Baltimore, Maryland (6/13/11).


M. C. Hersam, “Molecular-scale tailoring of graphene surface chemistry via organic functionalization,” presented orally by M. C. Hersam at the 219th Electrochemical Society Meeting, Montreal, Canada (5/3/11).

M. C. Hersam, “Fundamentals and applications of monodisperse carbon nanomaterials,” presented orally by M. C. Hersam at the 219th Electrochemical Society Meeting, Montreal, Canada (5/2/11).


M. C. Hersam, “Fundamentals and applications of monodisperse carbon-based nanomaterials,” presented orally by M. C. Hersam at the 2011 American Physical Society March Meeting, Dallas, Texas (3/21/11).


M. C. Hersam, “Chemically enhanced carbon-based nanoelectronic materials and devices,” presented orally at the International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii (12/18/10).


M. C. Hersam, “Chemically tailoring graphene via organic self-assembled monolayers,” presented orally at the 57th AVS International Symposium, Albuquerque, New Mexico (10/19/10).

M. C. Hersam, “Blurring the boundaries: Opportunities for medicine at the interface between the physical and life sciences,” presented orally at the Alumnae Continuing Education Forum, Evanston, Illinois (10/14/10).


M. C. Hersam, “Fundamentals and applications of monodisperse carbon-based nanomaterials,” presented orally at the 4th NIST Carbon Nanotube Workshop, Gaithersburg, Maryland (9/23/10).

M. C. Hersam, “Molecular-scale tailoring of graphene surface chemistry via organic functionalization,” presented orally at the Workshop on Carbon Based Electronics, Albany, New York (9/22/10).

M. C. Hersam, “Chemically enhanced carbon-based nanomaterials and devices,” presented orally at the Purdue University Department of Chemistry Colloquium, West Lafayette, Indiana (9/9/10).

M. C. Hersam, “Ultra-high vacuum processing and characterization of chemically functionalized graphene,” presented orally at the 18th International Vacuum Congress and International Conference on Nanoscience and Technology, Beijing, China (8/24/10).


M. C. Hersam, “Preparation, characterization, and application of monodisperse carbon-based nanomaterials,” presented orally at the...
C. Hersam at the 2010 ChemOnTubes Conference, Arcachon, France (4/12/10).


*[40] M. C. Hersam, “Enhancing carbon-based nanomaterials and devices via chemical processing,” presented orally by M. C. Hersam at the Case Western Reserve University Department of Chemical Engineering Seminar Series, Cleveland, Ohio (2/18/10).


M. C. Hersam, “Preparation and characterization of monodisperse carbon nanotube materials and devices,” presented orally by M. C. Hersam at the Hillsdale College Department of Chemistry Seminar Series, Hillsdale, Michigan (2/24/09).


M. C. Hersam, “Preparation and characterization of monodisperse carbon nanotube materials and devices,” presented orally by M. C. Hersam at the University of California at Irvine Chemical Engineering and Materials Science Colloquium, Irvine, California (2/6/09).


M. C. Hersam, “Introduction to nanometer scale science and technology,” presented orally by M. C. Hersam at Schiff Hardin LLP, Chicago, Illinois (1/15/09).

M. C. Hersam, “Introduction to nanometer scale science and technology,” presented orally by M. C. Hersam at the Nanotechnology Town Hall Meeting, Evanston, Illinois (12/2/08).

M. C. Hersam, “Preparation and characterization of high purity single-walled and double-walled carbon nanotubes,” presented orally by M. C. Hersam at the 2008 Materials Research Society Fall Meeting, Boston, Massachusetts (11/30/08).


M. C. Hersam, “Alternative energy opportunities for high purity carbon nanomaterials,” presented orally by M. C. Hersam at the Joint India-US Workshop on Scalable Nanomaterials for Enhanced Energy Transport, Conversion, and Efficiency, Bangalore, India (8/19/08).

M. C. Hersam, “Size-dependent properties: Opportunities and obstacles for nanomaterials,” presented orally by M. C. Hersam at the Symposium Toward a Strategic Vision for Chemical and Biological Defense, Atlanta, Georgia (8/7/08).

M. C. Hersam, “Progress towards monodisperse carbon nanotubes,” presented orally by M. C. Hersam at the Virtual Conference on Nanoscale Science and Technology, Fayetteville, Arkansas (7/25/08).


M. C. Hersam, “Preparation and characterization of monodisperse carbon-based nanomaterials,” presented orally by M. C. Hersam at the 2nd International Workshop on Metrology, Standardization, and Industrial Quality of Nanotubes, Montpellier, France (6/28/08).

M. C. Hersam, “Probing the structure and properties of individual molecules on silicon surfaces,” presented orally by M. C. Hersam at the 52nd International Conference on Electron, Ion, and Photon Beam Technology and Nanofabrication, Portland, Oregon (5/30/08).

M. C. Hersam, “Tuning the electrical and optical properties of monodisperse carbon-based nanomaterials,” presented orally by M. C. Hersam at the 213th Electrochemical Society Meeting, Phoenix, Arizona (5/19/08).


M. C. Hersam, “Probing and manipulating surface chemistry with scanning probe microscopy,” presented orally by M. C. Hersam at the Army Research Office Organic and Inorganic Chemistry Workshop, Boston, Massachusetts (3/19/08).

M. C. Hersam, “Preparation, characterization, and applications of monodisperse single-walled carbon nanotubes,” presented orally by M. C. Hersam at the 22nd International Winterschool on Electronic Properties of Novel Materials, Kirchberg, Austria (3/6/08).

M. C. Hersam, “Tuning the electrical and optical properties of monodisperse carbon-based nanomaterials,” presented orally by M. C. Hersam at the Yonsei Global Engineering Symposium, Seoul, Korea (2/14/08).

M. C. Hersam, “Preparation and application of high purity carbon-based nanomaterials,” presented orally by M. C. Hersam at the Seoul National University Department of Physics Colloquium Series, Seoul, Korea (2/13/08).

M. C. Hersam, “Single molecule chemistry on silicon surfaces characterized by ultra-high vacuum scanning tunneling microscopy,” presented orally by M. C. Hersam at the Ajou University Molecular Science and Technology Seminar Series, Suwon, Korea (2/12/08).

M. C. Hersam, “Tuning the electrical and optical properties of monodisperse carbon-based nanomaterials,” presented orally by M. C. Hersam at the Ajou University Molecular Science and Technology Seminar Series, Suwon, Korea (2/12/08).

M. C. Hersam, “Production and application of high purity carbon-based nanomaterials,” presented orally by M. C. Hersam at the University of Illinois at Chicago Department of Mechanical and Industrial Engineering Colloquium Series, Chicago, Illinois (1/22/08).


M. C. Hersam, “Probing the structure and properties of individual molecules on silicon surfaces,” presented orally by M. C. Hersam at the University of Albany College of Nanoscale Science and Engineering Colloquium Series, Albany, New York (12/7/07).

M. C. Hersam, “Recent developments and applications of high purity carbon nanomaterials,” presented orally by M. C. Hersam at the Rensselaer Polytechnic Institute Department of Materials Science and Engineering Colloquium Series, Troy, New York (12/6/07).


M. C. Hersam, “Sorting single-walled carbon nanotubes by their physical and electronic structure using density differentiation,”
presented orally by M. C. Hersam at the 3rd NASA-NIST Workshop on Nanotube Measurements, Gaithersburg, Maryland (9/26/07).

*[93] M. C. Hersam, “Structure, properties, and processing of chirality-resolved single-walled carbon nanotubes,” presented orally by M. C. Hersam at the University of Arkansas at Little Rock Joint College Colloquium Series, Little Rock, Arkansas (9/14/07).


*[103] M. C. Hersam, “Hybrid organic/inorganic nanomaterials: Characterization, processing, and applications,” presented orally by M. C. Hersam at the Kenyon College Department of Physics Colloquium, Gambier, Ohio (4/23/07).


*[110] M. C. Hersam, “Introduction to nanometer scale science and technology,” presented orally by M. C. Hersam at the Ajou University Molecular Science and Technology Seminar Series, Suwon, Korea (2/26/07).
M. C. Hersam, “Purification and optical properties of biofunctionalized carbon nanotubes: Implications for multi-analyte sensing,” presented orally by M. C. Hersam at the SPIE Photonics West Meeting, San Jose, California (1/25/07).

M. C. Hersam, “Introduction to nanometer-scale science and technology,” presented orally by M. C. Hersam at the American Society for Mechanical Engineers Chicago Chapter Meeting, Evanston, Illinois (1/9/07).

M. C. Hersam, “Sorting single-walled carbon nanotubes via density gradient centrifugation,” presented orally by M. C. Hersam at the Nano Business Alliance Seminar Series, Skokie, Illinois (12/12/06).


M. C. Hersam, “Probing molecular electronics with scanning probe microscopy,” presented orally by M. C. Hersam at the Pan-American Advanced Studies Institute Program on Nano and Biotechnology, Bariloche, Argentina (11/20/06).

M. C. Hersam, “Nanoelectronics: Device physics and fabrication technology,” presented orally by M. C. Hersam at the Pan-American Advanced Studies Institute Program on Nano and Biotechnology, Bariloche, Argentina (11/20/06).


M. C. Hersam, “Probing chemistry and electronic structure at the single molecule level with scanning tunneling microscopy,” presented orally by M. C. Hersam at the Tufts University Department of Chemistry Colloquium, Medford, Massachusetts (10/3/06).

M. C. Hersam, “Electrical contacts at the nanometer scale,” presented orally by M. C. Hersam at the 52nd IEEE Holm Symposium, Montreal, Canada (9/27/06).

M. C. Hersam, “Probing the dynamics of individual molecules on silicon surfaces with ultra-high vacuum scanning tunneling microscopy,” presented orally by M. C. Hersam at the ACS Fall Meeting, San Francisco, California (9/11/06).


M. C. Hersam, “Probing molecular electronics with scanning probe microscopy,” presented orally by M. C. Hersam at the National Science Foundation Summer Institute on Micro and Nano Devices with Applications to Biology and Nanoelectronics, Evanston, Illinois (8/10/06).
[129] M. C. Hersam, “Nanoelectronics: Device physics and fabrication technology,” presented orally by M. C. Hersam at the National Science Foundation Summer Institute on Micro and Nano Devices with Applications to Biology and Nanoelectronics, Evanston, Illinois (8/10/06).

[130] M. C. Hersam, “Ultra-high vacuum scanning tunneling microscopy studies of single molecules on semiconductor surfaces,” presented orally by M. C. Hersam at the International Conference on Nanoscience and Technology, Basel, Switzerland (8/2/06).


[133] M. C. Hersam, “Introduction to nanoelectronics,” presented orally by M. C. Hersam at the ASME Nano Training Bootcamp, St. Paul, Minnesota (7/13/06).


[135] M. C. Hersam, “Probing organic chemistry on silicon surfaces at the single molecule level with ultra-high vacuum scanning tunneling microscopy,” presented orally by M. C. Hersam at the University of California at Riverside Chemistry Department Colloquium, Riverside, California (6/7/06).


[138] M. C. Hersam, “Atomic resolution patterning of organosilicon heteromolecular nanostructures using feedback controlled lithography,” presented orally by M. C. Hersam at the ACS Spring Meeting, Atlanta, Georgia (3/26/06).


[144] M. C. Hersam, “Separation of single-walled carbon nanotubes by diameter using density gradient centrifugation,” presented orally by M. C. Hersam at the FACSS 51st International Conference on Analytical Sciences and Spectroscopy, Quebec City, Canada (10/10/05).

M. C. Hersam, “Purification and optical properties of biofunctionalized carbon nanotubes,” presented orally by M. C. Hersam at the Materials Science and Technology 2005 Conference, Pittsburgh, Pennsylvania (9/28/05).

M. C. Hersam, “Probing single molecule charge transport on silicon surfaces using scanning tunneling microscopy,” presented orally by M. C. Hersam at the Bat Sheva Seminar on Electron Transport in Molecular Junctions, Mizpe Hayamim, Israel (9/18/05).


M. C. Hersam, “Introduction to nanoscale science and technology,” presented orally by M. C. Hersam at the Khon Kaen University School of Pharmacy Colloquium, Khon Kaen, Thailand (8/10/05).

M. C. Hersam, “Single molecule sensing, characterization, and actuation,” presented orally by M. C. Hersam at the International Materials Research and Nanotechnology Workshop, Khon Kaen, Thailand (8/8/05).


M. C. Hersam, “Introduction to nanoelectronics,” presented orally by M. C. Hersam at the ASME Nano Training Bootcamp, Washington, D.C. (7/14/05).


M. C. Hersam, “Introduction to nanometer scale science and technology,” presented orally by M. C. Hersam at the American Institute of Chemical Engineering Chicago Section Symposium, Chicago, Illinois (4/20/05).

M. C. Hersam, “Probing electronic properties at the single molecule level on silicon surfaces,” presented orally by M. C. Hersam at the Yale University Solid State and Optics Seminar Series, New Haven, Connecticut (4/13/05).

Number of Presentations: 155.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received   Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received   Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts


TOTAL: 2

Books

Patents Submitted


Patents Awarded


Awards

[1] AVS Prairie Chapter Award for Outstanding Research, 2011
[2] Teacher of the Year in the Department of Materials Science and Engineering, 2010
[4] SES Research Young Investigator Award, Electrochemical Society, 2010
[5] Senior Member, Institute of Electrical and Electronics Engineers, 2009
[7] Young Alumni Achievement Award, ECE Department, UIUC, 2007
[8] AVS Peter Mark Award, 2006
[9] TMS Robert Lansing Hardy Award, 2006
[10] Chicago Area Undergraduate Research Symposium Faculty Research Award, 2006
[12] Alfred P. Sloan Research Fellowship, 2005

Graduate Students

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Student Metrics

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The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields: ...... 2.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale): ...... 2.00
Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering: ...... 0.00
The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense ...... 0.00
The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: ...... 2.00

Names of Personnel receiving masters degrees

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Sub Contractors (DD882)
5 System and methods of laser assisted field induced oxide nanopatterning

Patent Filed in US? (5d-1) Y
Patent Filed in Foreign Countries? (5d-2) N
Was the assignment forwarded to the contracting officer? (5e) N
Foreign Countries of application (5g-2):

5a: Liam S. C. Pingree
5f-1a: Northwestern University
5f-c: 2220 Campus Drive
      Evanston   IL   60208

5a: Mark C. Hersam
5f-1a: Northwestern University
5f-c: 2220 Campus Drive
      Evanston   IL   60208

Scientific Progress

See Attachment

Technology Transfer
Scientific Progress and Accomplishments

1. Scanning Ion Conductance Microscopy of Electrochemically Active Electrodes

Prior work has established scanning ion conductance microscopy (SICM) as an important technique for nanoscale characterization in aqueous electrolytes. SICM is an entirely non-contact method, which provides distinct advantages for topographical imaging of delicate structures such as biological cells in liquids. SICM can also be combined with scanning electrochemical microscopy (SECM) to add further electrochemical capabilities beyond topographic mapping. Since SICM directly measures ion currents through a nanoscale pipette, it is well suited for simultaneous imaging of topography and ion currents, as has been previously shown for porous membranes. In order to obtain these spatially resolved ion currents, the SICM is implemented in a loose patch clamp geometry where the pipette is brought close to the sample to form a low resistance seal. Over the past year, we have employed SICM as a tool for concurrently imaging the topography and local Li⁺ ion currents on battery electrode materials. This in situ characterization reveals the evolution of spatial inhomogeneities in the structure and electrochemical activity of the substrate as a function of lithiation state, thus providing unique nanoscale insight into the operation of Li-ion batteries.

Since SICM is a technique originally developed for biological samples, many modifications were made to the SICM apparatus to enable imaging of battery electrodes in situ. Figure 1 shows a schematic of the SICM configuration used in this study. The electrically grounded sample is mounted in a petri dish, which is then filled with the battery electrolyte. A glass pipette, pulled to the desired diameter, is filled with the same electrolyte, and a lithiated tin wire is placed inside. Lithiated tin is used as the source of Li⁺ ions instead of lithium metal as similarly sized lithium wire was not mechanically robust enough to survive the pipette insertion process.
Figure 1. Schematic diagram of the in situ Li-ion battery SICM configuration. The entire apparatus is housed inside of an argon filled glovebox, which permits the use of electrolytes that are employed in actual Li-ion batteries.

Once the pipette is lowered into the electrolyte in the petri dish, a Li\(^+\) ion current flows from the tip into the sample. As the tip approaches the sample, the seal resistance increases between the pipette and the electrode material that is not directly beneath the tip. Since the majority of the original current is supplied by the surrounding electrode material, the current at a constant voltage decreases as the tip approaches the sample. When the tip is oscillated vertically, the magnitude of the alternating current (AC) at the driving frequency monotonically increases as the tip approaches the sample. In this manner, the magnitude of the AC current can be used as the feedback signal to maintain a constant tip-sample spacing. Since a constant tip-sample spacing implies a constant average seal resistance, the current remains constant between the pipette and the sample beyond the local region of the tip. Consequently, changes to the overall current during scanning are predominantly attributed to spatial variations in the ionic current.

Spatial inhomogeneity in the ionic current can be caused by a number of factors. Ideally, current should be generated equally throughout the volume of the electrode material. In this case, the local ionic current will be proportional to the electrode material thickness, implying a direct relationship between sample thickness and ionic current. On the other hand, if a region of the electrode is inactive or less active due to poor electrical contact to the current collector, a reduction in current can be expected. Similarly, barriers to lithiation such as the formation of a relatively impervious solid electrolyte interphase (SEI) layer will also reduce the local ionic current. In a real battery electrode, the ionic current will be a convolution of these effects.

To determine the relative importance of these potentially competing contributions to the ionic current, a variety of test samples were characterized with SICM. Initially, silicon nanoparticles mixed with poly(vinylidene difluoride) (PVDF) deposited on copper foil were prepared to illustrate current contrast based on sample thickness. The drop-casting conditions were adjusted to ensure high surface roughness and corresponding variability in sample thickness. The resulting SICM topography and current images are shown in Figure 2. The measured current is higher over topographically protruding regions since all of the nanoparticles throughout the sample thickness can participate in lithiation. Reduced current is also observed around the protruding features, which is likely due to a local depletion in Si nanoparticles as they are incorporated into the larger agglomerate during drop-casting.
Figure 2. SICM (a) topography image and (b) DC current map of silicon nanoparticles and PVDF deposited via drop-casting on copper foil.

To directly compare electrochemically active and inactive materials, tin stripes were fabricated on a copper thin film on glass. The resulting SICM images of this lithographically defined sample are shown in Figure 3. A clear increase in current is detected over the regions of the tin stripes as expected. In particular, Figure 3c shows the extracted profile perpendicular to the stripe, which has been averaged over 128 pixels. In addition to the increased current in the flat region of the tin stripe, imaging artifacts characteristic of cross-talk between topography and current are observed to the left and right of the stripe. Since the fast scan direction is from left to right, the pipette approaches a steep incline on the left side and a steep drop on the right side of the tin stripes. The finite response time of the feedback system implies that the tip is closer to the surface than the setpoint on the left side and further away on the right, leading to the observed drop in current on the left and slight increase in current on the right. Increasing data acquisition time (i.e., reducing scan speed) allows this effect to be minimized.

Figure 3. SICM of tin stripes on 60 nm of copper on glass: (a) topography image, (b) DC current map, and (c) extracted profile averaged over 128 pixels parallel to the stripes.
To explore a more realistic battery electrode, a tin thin film was evaporated on a copper thin film on glass. These as-deposited films naturally possess topographical corrugation exceeding 10 nm as can be seen in Figure 4a. The contrast in the corresponding SICM current map in Figure 4b is dominated by thickness variations in a similar fashion to the silicon nanoparticle composite shown in Figure 2. After partial lithiation of 24 μAh cm⁻² at 24 μA cm⁻², significant structural changes are observed in Figures 4c and 4d. In particular, local regions have undergone clear increases in topography, likely due to catalytic decomposition of the electrolyte. Overall, the current has increased over these features, which is consistent with their preferential growth.

A closer evaluation of these images provides further insight into the growth process. Extracted profiles along the yellow and green lines of Figures 4c and 4d are shown in Figure 5. In particular, Figure 5a shows a drop in current that is apparent around the topographically protruding feature. This peripheral reduction in current suggests an SEI that partially seals regions around the growing features, thereby concentrating ionic current. The profile in Figure 5b demonstrates that topographically high features do not necessarily correlate with regions of increased current. For example, the feature indicated by the black arrow has a similar topographic height to the other protruding features, but the corresponding current is only as high as regions in the background. This observation suggests that the growing film can eventually block the tin electrode underneath such that the electrolyte can no longer access it and catalytically decompose. Once the catalytic decomposition has ended, the current will be due to lithiation and normal SEI formation as is seen in the background.

![Figure 4](image_url)

**Figure 4.** SICM (a,c) topography and (b,d) DC current images of a 60 nm thick tin thin film deposited on a 60 nm thick copper thin film on glass (a,b) before lithiation and (c,d) after 24μAh cm⁻² lithiation.
In summary, it has been demonstrated that SICM is an effective in situ technique for studying both the topography and electrochemistry of battery electrode materials at the nanoscale. Correlated topographic and current mapping of test structures reveals a number of factors that lead to spatial inhomogeneities including thickness of the active battery material and barriers to lithiation including the evolution of the SEI. Subsequent measurements on tin electrodes provide a nanoscale picture of catalytic decomposition of the electrolyte where an SEI is observed to form around electrode regions that rapidly grow during lithiation. In addition, the lithiation process can induce local film growth to the point where further electrolyte decomposition is suppressed. Overall, this work establishes the unique capabilities of SICM as an in situ tool for probing spatial inhomogeneities in topography and electrochemistry in battery electrodes, thus providing new characterization data that can inform ongoing efforts to understand and improve the capacity, lifetime, and safety of lithium ion battery technology.

2. Quantification of SECM-SICM in Both DC and AC Modes

In recent years, scanning ion conductance microscopy (SICM) has emerged as a versatile noncontact imaging tool. As such, SICM can be applied to numerous biophysical systems, including proteins in cell membranes, suspended artificial membranes, ionic conductivity of porous membranes, and mechanical properties of living cells. In addition, the capabilities of SICM have been extended by integrating complementary techniques, including confocal microscopy, scanning near field optical microscopy (SNOM), and patch clamping. These auxiliary measurements provide additional information about the sample that is correlated with
the surface topography detected by SICM imaging. Despite these impressive advancements in SICM, it remains insensitive to electrochemical properties. Spatial mapping of electrochemistry is commonly achieved by scanning electrochemical imaging (SECM) and has been widely used in the study of electrode surfaces, membrane transport, and biological systems. In previous work, we advanced the capabilities of SICM for electrochemical imaging by developing and qualitatively demonstrating a nanopipette probe with an integrated ultramicroelectrode (UME) for concurrent SICM and SECM imaging. Over the past funding period, we have expanded this effort by performing quantitative SECM-SICM in both DC and AC modes.

Approach curves confirm both the feedback response of the integrated UME as it approaches a surface and the independence of the ion and redox current signals. Figure 6 and Figure 7 show the variations in the DC and AC components of the ion and redox currents on approach to a conducting gold surface and an insulating Teflon surface, respectively. In both cases, the DC currents are normalized with respect to their values measured far from the surface.

**Figure 6.** Approach curves to a conducting gold surface collected in 10 mM Ru(NH$_3$)$_6^{3+}$ with 100 mM KNO$_3$ supporting electrolyte. (A) Normalized DC ion current and AC ion current response. (B) Normalized DC redox current and AC redox current response.
Figure 7. Approach curves to an insulating Teflon surface collected in 10 mM \( \text{Ru(NH}_3\text{)_6}^{3+} \) with 100 mM KNO\(_3\) supporting electrolyte. (A) Normalized DC ion current and AC ion current response. (B) Normalized DC redox current and AC redox current response.

The DC ion current exhibits similar behavior on approach to either surface. This observation is consistent with the SICM feedback, which depends solely on the hindered diffusion of ionic species to the nanopipette tip and is substrate independent. The AC ion current is also consistent with expectations, with an increased AC component upon approach. At large tip-sample distances, the ion current is unperturbed by the relatively small oscillation amplitude of the probe. However, as the probe approaches the surface and the oscillation amplitude become significant relative to the tip-sample spacing, this ac component increases in magnitude.

On the other hand, the redox current exhibits substrate dependent behavior on approach to conducting and insulating surfaces, consistent with the SECM feedback mechanism. As the integrated UME approaches a conducting gold surface, the DC current increases due to recycling of the UME-generated species. Conversely, as the probe approaches an insulating Teflon surface, the DC current decreases due to hindered diffusion to the UME. Similarly, the AC current also depends upon surface conductivity. Like the ion current, the redox current has no AC component at large tip-sample spacings and increases on approach to the surface. However, the AC redox current response to conducting and insulating surfaces are 180° out of phase. This phase shift can be explained by approximating the AC response as the derivative of the DC response. Positive feedback over conducting surfaces results in increased DC current and positive AC response, while negative feedback over insulating surfaces results in decreased DC current and negative AC response.

The AC redox current has significant advantages over the DC redox current as an electrochemical imaging signal. As shown in Figure 6 and Figure 7, the AC signal is more surface-sensitive than the DC signal, with variations occurring at smaller tip-sample spacings relative to the DC signal. Furthermore, the AC signal eliminates the large DC offset current associated with the steady-state response of the UME, making small variations in the ac current easier to detect than small variations in the dc current. This effect has implications for the probe
fabrication as well. With DC current, any defects in the probe’s insulating film produce an increased DC offset current, which complicates small signal detection. However, the AC current will remain insensitive to many of these defects, as defects far from the tip will be too far from the surface to generate an AC response. This reduced sensitivity to defects is useful, as the deposition of a high-quality, pinhole free insulating film is one of the primary challenges in fabricating SECM probes.

3. Templating Iridium Oxide Nanostructured Electrodes in AAO Membranes

Iridium oxide (IrOx) has been studied and utilized for a wide range of applications including electrochromic devices, pH sensing, and neural stimulation. IrOx is particularly well-suited for neural stimulation due to the large charge storage capacities associated with faradaic reactions between Ir$^{3+}$ and Ir$^{4+}$ redox states within the oxide. 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. IrOx films have also been synthesized by a number of deposition strategies, including sputtering and electrodeposition. 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 and sputtered IrOx films.

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 and have been widely used to prepare nanoporous materials. ALD is a deposition technique utilizing iterative, self-limiting surface reactions to deposit thin films in a monolayer-by-monolayer fashion that enables films with precise thickness and compositional control, high conformality, and uniform infiltration of porous templates. Detailed synthetic procedures and thorough experimental characterization are presented below, thus establishing the advantages of nanoporous AIROFs for charge storage and pH sensing applications.

AAO templates consisting of 350 nm diameter, 18 µm long pores with 425 nm spacing were prepared using a two-step anodization procedure. Anodizations were conducted at 170 V in 0.3 M H$_3$PO$_4$ at 5°C and exhibited a growth rate of 0.3 µm/min. Following anodization, pores were widened by etching in 10 wt% H$_3$PO$_4$ at 35°C for 1 hour.

Flat and nanoporous Ir films were prepared by ALD onto glass and AAO templates, respectively. Ir ALD was conducted in a viscous flow reactor 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°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 Å Al$_2$O$_3$ film was then deposited as a nucleation layer by iterative exposures of trimethylaluminum and H$_2$O. Ir films were then deposited by iterative exposures of iridium(III) acetylacetonate (Ir(acac)$_3$), maintained within a stainless steel bubbler at a 170°C and O$_2$. Ir ALD was conducted with 5-10
sec Ir(acac)\textsubscript{3} exposures and 2 sec O\textsubscript{2} exposures, with each exposure followed by a 5 sec N\textsubscript{2} purge. All Ir films were deposited for 600 cycles and were \textasciitilde 27 nm thick.

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 potential cycling in 0.1 M H\textsubscript{2}SO\textsubscript{4} between –0.7 and 0.8 V vs. mercury/mercurous sulfate electrode (MSE) at a scan rate of 100 mV/s. Immediately following activation, the AIROFs were characterized by cyclic voltammetry (CV) in 1 M H\textsubscript{2}SO\textsubscript{4} between –0.7 and 0.8 V vs. MSE at a scan rate of 100 mV/s. The cathodal charge storage capacity (CSC\textsubscript{c}), which provides a measure of the total charge stored within the IrO\textsubscript{x} film and available for a stimulation pulse, was determined by CV between –0.6 and 0.8 V vs. Ag/AgCl in phosphate-buffered saline solution (22 mM NaH\textsubscript{2}PO\textsubscript{4}, 81 mM Na\textsubscript{2}HPO\textsubscript{4}, and 130 mM NaCl). The CSC\textsubscript{c} was calculated as the time integral of the negative current over a complete CV cycle.

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 H\textsubscript{2}O for at least 12 hours prior to pH testing.

The nanoporous Ir metal films prepared by ALD into AAO templates are shown in Figure 8. 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)\textsubscript{3} exposure time, with 5 and 10 sec exposure times resulting in infiltration depths of 2.2 and 9 µm, respectively. Additionally, as shown in Figure 8E, 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.
Figure 8. 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 sec Ir(acac)$_3$ exposures and D) 10 sec Ir(acac)$_3$ exposures. E) CV in 1 M H$_2$SO$_4$ of flat and nanoporous Ir films demonstrating the surface area enhancement of the nanoporous films.

Nanoporous AIROFs are prepared by potential cycling in 0.1 M H$_2$SO$_4$. As shown in Figure 9A, 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. 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.

Figure 9. 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 CSCc.

The AIROFs are also characterized by CV in 1 M H2SO4. As shown in Figure 9B, 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 Figure 9C, the nanoporous AIROFs exhibit enhanced CSCc, with the 5 and 10 sec Ir(acac)3 nanoporous AIROFs exhibiting 127 and 311 mC/cm2, respectively, and the flat AIROF exhibiting 18.7 mC/cm2. The large CSCc of nanoporous AIROFs is highly desirable, as more charge can be delivered per stimulation pulse. However, the magnitude of the CSCc is also significant with regards to mechanical stability. With more conventional AIROFs formed on Ir thin films or foils, large CSCc values are commonly achieved by forming thicker IrOx films. However, these thicker IrOx film are more likely to exhibit delamination or other mechanical failures, especially at CSCc > 80 mC/cm2. However, the nanoporous AIROFs are less susceptible to these problems, as the primary factor determining CSCc 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 CSCc 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 CSCc after being subjected to ultrasonication treatments. The ability to achieve large CSCc with thin IrOx films also has significant practical advantages, in that fewer activation cycles are required, which allows for quicker fabrication of such films.
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 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, the super-Nernstian response indicates that the AIROFs are at least partially hydrous in nature, which is consistent with AIROF synthesis.

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 CSC₆ 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.

4. Development and Demonstration of SECM-SICM Imaging

In recent years, scanning ion conductance microscopy (SICM) has emerged as a versatile “non-contact” imaging tool. As such, SICM has been applied to numerous biophysical systems, including proteins in cell membranes, suspended artificial membranes, ionic conductivity of porous membranes, and mechanical properties of living cells. In addition, SICM has been further developed by integrating complementary techniques, including confocal microscopy, scanning near field optical microscopy (SNOM), and patch clamping. These auxiliary measurements provide additional information about the sample that is correlated with the surface topography detected by SICM imaging. Despite these impressive advancements in SICM, it remains insensitive to electrochemical properties. Spatial mapping of electrochemistry is commonly achieved by scanning electrochemical imaging (SECM) and has been widely used in the study of electrode surfaces, membrane transport, and biological systems. Over the past year, we have advanced the capabilities of SICM for electrochemical imaging by developing and demonstrating a nanopipette probe with an integrated ultramicroelectrode (UME) for concurrent SICM and SECM imaging.

The SECM-SICM probe fabrication procedure is shown in Figure 10. Nanopipettes were pulled from borosilicate glass capillaries (1 mm outer diameter, 0.5 mm inner diameter with filament, Sutter Instruments, Novato, CA) with a CO₂ laser-based pipette puller (P-2000, Sutter Instruments). Through experimentation with puller recipes, the pipette tips were consistently 200 nm in diameter with a 100 nm diameter opening, as measured by scanning electron microscopy (SEM). A 200-250 nm gold electrode film with a 5 nm titanium adhesion layer was electron beam evaporated onto one side of the pipette. The gold-coated pipette was then insulated by 70-100 nm of Al₂O₃ deposited by atomic layer deposition (ALD) in a viscous flow
type reactor. Al₂O₃ films were deposited at a temperature of 200°C with trimethylaluminum and H₂O reactants iteratively pulsed into the reactors at dose times of 1 second and purge times of 5 seconds. The Al₂O₃ deposition rate was approximately 0.105 nm/cycle. Lastly, the pipettes were focused ion beam (FIB) milled to expose the gold film as a UME and ensure an open pipette tip. FIB milling was conducted in a dual-beam FIB (FEI Helios, Hillsboro, OR) with a 30 kV, 0.28 pA ion beam. Pipettes were mounted gold side down onto the stage with conductive copper tape to ensure electrical contact to the pipette and minimize charging during image and milling. Milling was conducted normal to pipette axis in a multi-step process. The pipette was first milled to an outer diameter of approximately 800 nm. SEM imaging was then used to confirm that the UME was exposed and that the pipette tip was open. After confirmation, a final single pass milling step was used to clean the exposed microelectrode surface.

![Figure 10. Scanning electron microscopy images of the SECM-SICM nanopipette at different points in the fabrication process. (A) After pipette pulling with 30 nm AuPd film to minimize charging. (B) After evaporation of the Ti/Au electrode film. (C) After atomic layer deposition of a 100 nm thick Al₂O₃ film. (D) After focused ion beam milling to open the nanopipette and expose the Au ultramicroelectrode.](image-url)

A schematic of the SECM-SICM instrumentation is shown in Figure 11. SICM imaging was achieved with a commercially available SICM instrument (ScanIC, ionscope, London, U.K.). The pipette was mounted onto a single-axis piezo scanner for pipette oscillation and feedback-controlled movement of the pipette in the z direction. Samples were placed into a small petri dish filled with solution. The petri dish rests on a separate piezo scanner that rasters in the x and y directions for SICM imaging. The entire SICM microscope rests above an inverted optical microscope stage for positioning of the pipette relative to the sample.
Conventional SICM imaging utilizes two electrodes. A Ag/AgCl electrode in the bath solution was grounded and served as the reference electrode for all applied voltages, and a separate Ag/AgCl electrode was placed inside of the pipette and biased to generate an ion current through the pipette tip. This ion current was amplified, with the AC component of the ion current detected by the SICM hardware and serving as the feedback signal for topographic imaging. For integrated SECM-SICM imaging, a third electrode connection was made to the UME. Voltages were applied and the redox current was amplified by a low-noise patch-clamp amplifier (AxoPatch 200B, Molecular Devices, Sunnyvale, CA). The AC components of both the ion and redox currents at the pipette oscillation frequency were measured using two separate lock-in amplifiers (SR850, Stanford Research Systems, Sunnyvale, CA). A low-noise digitizer (Digidata 1440A, Molecular Devices) was used to apply all electrode biases and to monitor and record all signals.

Integrated SECM-SICM imaging has been demonstrated feedback mode imaging on patterned substrates. Feedback mode imaging was conducted on FIB-milled substrates in a solution of 10 mM Ru(NH₃)₆Cl₃, 100 mM KNO₃. Figure 12 shows SEM images of the fabricated test structures and corresponding SECM-SICM topography, DC redox current, and AC redox current images. The substrates consist of 400 nm wide trenches with a center-to-center spacing of 2.6 µm that were FIB-milled into a gold film to expose the underlying glass substrate. These recessed features are narrower than the overall diameter of the fabricated SECM-SICM probe, preventing the full extension of the probe into the trench; yet the trenches are still detected in the SICM topography image, indicating successful surface tracking via SICM feedback and allowing comparison between the topographic and electrochemical features.
Figure 12. SEM and feedback-mode SECM-SICM images of 400 nm wide trenches that were FIB-milled into a gold film to expose the underlying glass substrate. The images were taken in 10 mM Ru(NH$_3$)$_6^{3+}$, 100 mM KNO$_3$. (A) SEM, (B) SECM-SICM topography, (C) SECM-SICM DC redox current, (D) SECM-SICM AC redox current.

Correlation of the topography and redox current images reveals the expected contrast in both the DC and AC redox current images, with enhanced current over the broad Au regions, consistent with positive feedback, and reduced current over the narrow insulating trenches, consistent with negative feedback. As shown in the line profile in Figure 13, the redox current signals exhibit some convolution between the trench and UME dimensions, resulting in an observed full width at half maximum (FWHM) of 680 nm in the DC redox current and 580 nm in the AC redox current. Despite this broadening, the UME is capable of resolving the trenches as isolated features, with the redox current returning to a constant value between the trenches. The line profile also reveals a lateral offset between the topographic and redox current signals of approximately 230 nm, which is consistent with the center-to-center separation of the nanopipette tip opening and the integrated UME.
Figure 13. Line profile of the SECM-SICM topography, DC redox current and AC redox current on the 400 nm wide FIB-milled patterns from Figure 12.

As shown in Figure 14, SECM-SICM images were also acquired of 180 nm wide trenches separated by 875 nm to further characterize the spatial resolution of the probes. At these reduced dimensions, the probes are still capable of detecting the trenches in SICM topography, DC redox current, and AC redox current images. Despite the increased significance of the lateral broadening relative to the inter-trench spacing, the probes are still capable of resolving individual trenches. Based on these images, it is clear that the probes are capable of detecting features in the deep sub-micron regime.

Figure 14. SEM and feedback-mode SECM-SICM images of 180 nm wide trenches that were FIB-milled into a gold film to expose the underlying glass substrate. The images were taken in 10 mM Ru(NH$_3$)$_6^{3+}$, 100 mM KNO$_3$. (A) SEM, (B) SECM-SICM topography, (C) SECM-SICM DC redox current, (D) SECM-SICM AC redox current.
5. Fabricating and Characterizing Nanoporous AAO Membranes

Anodized aluminum oxide (AAO) is an ideal prototype substrate for studying ion transport through nanoporous membranes. For optimal performance, it is highly desirable to independently control the width, height, and spacing of the pores in AAO. AAO templates are typically fabricated through a two-step anodization process. In the first step, a disordered nanoporous alumina film is created following constant voltage anodization of aluminum. As the film grows, the pores self-order over a period of hours, leading to a hexagonally ordered arrangement at the sub-surface growth front. When this initial alumina film is removed, the resulting aluminum surface possesses a hexagonally ordered arrangement of pits. These pits serve as pore nucleation sites during the second anodization step, thus yielding a highly uniform and ordered nanoporous AAO film. This two-step procedure creates ordered nanoporous arrays in sulfuric, oxalic, malonic, and phosphoric acids at 25 V, 40 V, 130 V, and 195 V with inter-pore spacings of 63 nm, 100 nm, 250 nm, and 500 nm respectively. By modifying the anodization solution and using higher than self-ordering voltages, additional inter-pore spacings have been achieved, but these conditions are not well-suited to thin film anodization. Consequently, aluminum pretexturing is required to form ordered AAO with arbitrary inter-pore spacings.

A number of patterning techniques have been explored to create ordered pits in aluminum as a precursor to AAO. For example, imprinting techniques using a mold fabricated by interference lithography, self-assembly of nanoparticles, or anodization have been shown to be effective. However, these techniques utilize large pressures rendering them unsuitable for aluminum thin films on brittle substrates, such as glass or silicon. Alternatively, aluminum can be evaporated onto hexagonally ordered nanospheres and then cleaved from the substrate to create ordered pits. Other strategies have employed reactive ion etching (RIE) with masks of through-hole AAO and diblock copolymers to create a textured aluminum surface. While each of these techniques possesses distinct advantages compared to the traditional two-step anodization process, their limited process latitude presents challenges for the fabrication of nanoporous membranes with arbitrarily tunable inter-pore spacing, pore diameter, and aspect ratio.

On the other hand, nanosphere lithography (NSL) is a technique that has been widely utilized to create periodic nanostructures due to its simple processing and controllable periodicity. In NSL, nanospheres of polystyrene (PS) or other materials are self-assembled onto a substrate into a hexagonally close-packed monolayer. Nanospheres can be deposited by a variety of methods including spin coating, dip coating, and evaporation to create this ordered monolayer. By controlling the nanosphere diameter and surface chemistry, the monolayer periodicity and ordering can be widely tuned.

Over the past year, we have employed NSL to pre-texture aluminum films on a variety of substrates to create AAO films with tunable inter-pore spacing, pore diameter, and aspect ratio. First, an aluminum thin film of the desired thickness is deposited on a selected substrate by thermal evaporation (Figure 15A). The Al surface is then pretreated by spinning a solution of Triton-X 100 surfactant and water to increase its hydrophilicity, which has been shown to be important in nanosphere ordering. A nanosphere solution containing water, PS spheres, and Triton-X 100 for sphere diameters of 80 nm and 160 nm, or water, methanol, PS spheres, and Triton-X 100 for 240 nm diameter spheres is then spun onto the Al surface. This procedure results in a hexagonally close-packed monolayer of PS spheres (Figure 15B). The monolayer is
subsequently etched using RIE with a 3:2 mixture of Ar:O$_2$ to reduce the nanosphere diameter. At this point, tungsten is sputter deposited, and the spheres are removed by sonicating in toluene at 70ºC (Figures 15C-E), leaving a tungsten film with an ordered array of holes. The tungsten is then used as a mask for nitric and phosphoric acid etching of the aluminum to create ordered pits in the Al surface, which serve as templates for AAO. In particular, the textured Al surface is anodized in 0ºC phosphoric acid at 50 V, 100 V, and 150 V for sphere diameters of 80 nm, 160 nm, and 240 nm respectively. Finally, the tungsten is selectively removed in an aqueous solution of potassium ferricyanide (Figure 15F). This process has been successfully performed on glass, silicon, and silicon nitride surfaces.

**Figure 15.** Schematic diagrams (top view and cross-sectional view) of the NSL-based anodization procedure: (a) Aluminum coated substrate; (b) Monolayer of assembled polystyrene nanospheres; (c) Etched polystyrene nanospheres; (d) Deposited tungsten film; (e) Nanospheres removed to yield openings in the tungsten film; (f) Final anodized alumina film.

Scanning electron microscopy (SEM) micrographs of the completed structures in Figure 16 show the uniformity of the pore size and inter-pore spacing. The inter-pore spacing is measured to be 84 nm, 154 nm, and 234 nm with pore diameters of 33 nm, 57 nm, and 70 nm for 80 nm, 160 nm, and 240 nm diameter spheres respectively. The inter-pore spacings closely match the nominal initial sphere diameters as expected. The 80 nm diameter spheres exhibit reduced ordering compared to the larger sphere sizes since they possess higher polydispersity. The pore diameter can be widened controllably using 5% phosphoric acid to create any larger pore size. Furthermore, the pore aspect ratio can be controlled by varying the deposited Al
thickness as shown in Figure 17. The AAO thicknesses are 400 nm, 700 nm, and 1000 nm for a deposited Al thickness of 300 nm, 400 nm, and 500 nm respectively when using 240 nm diameter spheres. It should also be noted that the pores are straight and do not split.

Figure 16. Scanning electron microscope images of the final AAO nanopore structures fabricated using (a) 80 nm, (b) 160nm, and (c) 240 nm nanosphere diameters.
Figure 17. SEM cross-sectional images of the final AAO nanopore structures fabricated using 240 nm diameter nanospheres and (a) 300 nm, (b) 400 nm, and (c) 500 nm thick aluminum films.

Supported nanoporous membranes are fabricated using a process similar to that of Si₃N₄ membrane fabrication. A Si(100) substrate is first coated with low pressure chemical vapor deposition Si₃N₄ (Figure 18A). Subsequently, photolithography and RIE with CF₄ and O₂ are used to etch apertures in the back (unpolished) Si₃N₄ layer. Aluminum is then deposited on the front (polished) side of the substrate and the NSL procedure is used to create AAO (Figure 18B). The sample is then sealed into a Teflon holder with Viton gaskets such that only the back (unpolished) side is exposed. Substrate etching is achieved in KOH, which is an anisotropic etch for the {100} planes over the {111} planes. The etching is carried out until the etch stops at the top Si₃N₄ layer, which is detected by the appearance of optical transparency. RIE with CF₄ and O₂ removes the Si₃N₄, and finally the AAO barrier oxide layer is removed in 5% phosphoric acid (Figure 18C).

Figure 18. Schematic diagrams of the processing steps used to achieve nanoporous AAO membranes. The left column is the cross-sectional view, the middle column is the polished side of the wafer, and the right column is the unpolished side of the wafer. (a) Initial silicon nitride coated silicon substrate. (b) AAO is formed on the top surface using the NSL-based anodization procedure, and an opening is patterned in the silicon nitride on the back surface. (c) Final nanoporous structure following etching of the silicon substrate, silicon nitride film, and AAO oxide barrier layer.
A transmitted electron image of a nanoporous membrane created with 240 nm diameter spheres and a 400 nm thick deposited Al film is shown in Figure 19. The bright spots indicate through-hole pores in the image since the transmission of electrons is unimpeded. The through-hole pores are observed with a high coverage over the entire membrane. Furthermore, the low voltage secondary electron and transmitted electron images in Figures 19B-C do not detect any contrast over the pores. Due to the high surface sensitivity and low penetration depth of low energy electrons, these low voltage images confirm that the pores are indeed through-hole. To further show through-hole nanoporous behavior, ionic conductance measurements were performed before and after etching the AAO barrier layer. Prior to etching, the ionic conductance is less than 1 nS in aqueous 1 M KCl. On the other hand, after removal of the barrier layer, the ionic conductance increases by three orders of magnitude, revealing the through-hole nature of the pores. In particular, Figure 20 reveals that the ionic conductance plateaus for increasing values of the KCl concentration. Similar ionic conductance plateau behavior has been found both theoretically and experimentally for through-hole nanopores in polymer membranes.

![Figure 19](image1.png)

**Figure 19.** Scanning electron microscopy images of the completed nanoporous membranes viewed from the unpolished side of the wafer. (a) Transmitted electron image with 30 kV accelerating voltage of the entire membrane. (b) Image taken at 1 kV accelerating voltage using the secondary electron detector. (c) The same image as in part b except using the transmitted electron detector.

![Figure 20](image2.png)

**Figure 20.** Ionic conductance through an AAO nanoporous membrane as a function of KCl concentration.