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Structured Electrochemical Materials Fabricated from Directed Self-Assembly of Block Copolymers and Advanced Lithography

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Nanolithography has propelled faster computer chips and even smaller electronic devices, but this patterning technique has not seen widespread adoption for making structured electrochemical materials. A prominent nanopatterning platform championed by numerous semiconductor manufactures is block copolymer lithography. Block copolymers spontaneously self-assemble at the molecular level and they can be directed into long-range ordered, perfect structures via directed self-assembly. Hence, they are attractive candidates for systematic study relating nanostructure to charge-transfer kinetics and transport phenomena. This report highlights the use of block copolymers to study ionic conductivity in microphase separated polymer electrolyte films and for patterning bulk ion-exchange membranes and glassy carbon substrates.

Introduction

Patterning technologies have fueled the information technologies revolution over the past 50 years and it has been the main driver for Moore's Law of doubling the transistor density on a chip area about every two years. Today's patterning platforms form long-range ordered structures with sub-10 nanometer features over large areas (1). In some instances, large 300 mm wafers featuring such small periodic structures can be defect free and contain over 100 billion transistor devices (2). Based on the remarkable track record of advanced patterning techniques for data information and processing technologies, it is reasonable to ask whether or not advanced patterning can be extended to other technologies, such as electrochemical energy storage and conversion. The impetus for considering such an extension is predicated on two reasons:

i.) Exact patterning of electrochemical materials with perfect structures, or systematically introduced defects, offers the opportunity to provide valuable insights into the transport and kinetic mechanisms that occur within these materials. Performing controlled experiments that absolve imperfections and defects from the nanostructure will inevitably lead to clearer interpretations of electrochemical data and will accelerate the rationale design of new functional and resilient electrochemical materials.

ii.) Patterning is an important processing step in the manufacture of electrochemical power sources on a chip (e.g., interdigitated microsupercapacitors and microbatteries). Interdigitated cell designs for microbatteries and microsupercapacitors can have both large power and energy densities (3-5). Additionally, these techniques can also pattern bulk solid-electrolyte materials, like Nafion® (6), for sandwich cell designs - as found in proton exchange membrane fuel cells. However, most patterning techniques have been constrained to micron feature sizes. Nano-scale feature sizes offer significant improvement over micron-scale feature sizes because they facilitate substantially larger interfacial area values (7).

Optical lithography has been the main workhorse for patterning electrochemical materials or fabricating micro-battery or –supercapacitors on a chip. This well-established and convenient patterning platform is limited however to fairly large feature sizes at the micron level (or in some cases several hundreds of nanometers). Understanding physical transport or kinetic mechanisms at the molecular level calls upon patterning strategies capable of making structures at much smaller length scales – at the tens of nanometers length scale or smaller. One low cost nanolithography platform capable of achieving periodic patterns with sub-10 nm resolution is block copolymer lithography (8). Canonical diblock and triblock copolymers can spontaneously microphase separate generating periodic patterns of 3 to 50 nm with various geometries that include lines from lamellae structures, and dots and meshes generated from cylinder- and sphere-forming structures (9-11). These versatile macromolecular entities can be directed into long-range ordered structures (i.e., directed self-assembly) when combined with other, complementary lithography platforms such as deep ultraviolet (UV) lithography (an optical lithography patterning technique) or electron beam lithography (8). It is important to note that block copolymer lithography has been implemented for the production of fin-field effect transistors (Fin-FETs) for microprocessors and bit-patterned media for magnetic hard drive disks – both data information and processing technologies (1, 2, 12).

In the first part of this work, the principles of directed self-assembly of block copolymers was leveraged to produce microphase separated block copolymer electrolytes (BCEs) with different concentrations of connected, ion-conducting pathways (13). Maximizing the population of the ion conducting domains allowed a 2 to 3 fold improvement in ionic conductivity over disconnected domains. The second part of the work presents preliminary data on nanopatterning glassy carbon disks and ion-exchange membranes with benchmark electrocatalysts (e.g., either platinum or gold) using block copolymer lithography.

Experimental

Nafion® 20wt% ionomer solution was purchased from Ion Power, Inc. Dimethylformamide (DMF), toluene, methyl iodide, and isopropanol (IPA) were purchased from VWR International. Trimethylaluminum chloride (> 97% purity grade) for atomic layer deposition was acquired from Sigma Aldrich. The following block copolymers were purchased from Polymer Source: poly(styrene-*block*-methyl methacrylate) (PS*b*PMMA) with Mn values of 36.8k-38k (lamellae forming), 50k-32k (PMMA rich and cylinder forming), and poly(styrene-*block*-2-vinyl pyridine) (PS*b*P2VP) with Mn values of 40k-44k (lamellae forming). Perfluorinated anion exchange membrane (PFAEM) and ionomer solution (10wt% in 2-propanol/water mixture – 50:50 by volume) were kindly supplied by the National Renewable Energy Laboratory (NREL). Silicon wafers (P/Boron<100>) and (with 100 µm thick SiOx layer) were purchased from WRS Materials. Deionized water was generated by a Millipore A10 advantage system.

For part one of this work, the self-assembled block copolymer electrolytes were prepared as described in previous works (13, 14). For brevity, the process is as follows: interdigitated gold electrodes (IDEs) were fabricated on to silicon wafers with 100 µm thick SiOx layer using conventional optical lithography. The IDEs contained two contact pads, 22 teeth that were 8 mm longer and 100 µm wide with 100 µm spacing. A non-preferential, random copolymer brush of monohydroxy-terminated poly(styrene-*random*-2-vinyl pyridine) (synthesized via a similar procedure) (15) was grafted to the IDE surface. PS*b*P2VP block copolymers (2 wt% in toluene) was spincoated on top of the IDEs with the non-preferential brush at 4000 RPM for 45 seconds. The PS*b*P2VP was annealed in a custom-built solvent annealing chamber with acetone vapor for 2 hours and the solvent was rapidly evaporated from the samples with a high flow rate (156 sccm) of nitrogen. The ordered PS*b*P2VP, about 30 nm in thickness, on top of the IDEs was converted to BCE by exposing the samples to methyl iodide vapor to introduce ionic moieties via a Menshutkin reaction. The exposure time to methyl iodide dictated the extent of reaction. Ionic conductivity measurements were carried out using electrochemical impedance spectroscopy and an electric circuit equivalent model extracted the film resistance to determine the in-plane conductivity.

For the second part of the work, a crosslinkable, non-preferential mat (poly(styrene-*random*-glycidyl methyl methacrylate) (PS*r*PMMA*r*PG4 – as synthesized in the literature) (16) of varying styrene composition was applied to glassy carbon substrates or silicon wafers featuring Nafion® or PFAEM films. Nafion® ionomer solution was made by mixing 5 wt% Nafion® dispersion with DMF in a volume ratio of 8:1; PFAEM ionomer solution was made by mixing 10 wt% PFAEM ionomer solution with DMF in a volume ratio of 1:1. These ionomer solutions were drop casted on to silicon wafers. PS*r*PMMA*r*PG4 was dissolved in toluene to 0.25 wt% and spincoated on the substrates at 4000 RPM for 40 seconds. The substrates were transferred to a thermal annealing chamber under nitrogen atmosphere and the non-preferential mats were crosslinked at 200 °C for 10 minutes. Afterwards, PS*b*PMMA block copolymer solutions (1.5 wt% in toluene) were spincoated on the substrates with non-preferential mats at 4000 RPM for 45 seconds. The films were thermally annealed under nitrogen at 200 °C for 10 minutes. The ordered PS*b*PMMA block copolymer films were transformed into organic-inorganic (alumina) hard masks for subsequent pattern transfer using sequential infiltrate synthesis (*SIS*) via reactive ion etching (17). This process was carried out with a GEMSTAR™ benchtop atomic layer deposition (ALD) system. Main reaction cycle was performed at 130 °C with controlled nitrogen flow rate of 30 sccm. Each exposure of TMA is followed by the exposure of H_2O and a purge step to evacuate excessive reagents. Each TMA exposure was performed in three repeating pulse and delay manner for 5s/15s respectively. Each H_2O exposure was performed in three repeating pulse and delay manner for 5s/15s respectively. The exposure/purge process was repeated five times to achieve complete infiltration of precursor into PMMA domains of the block copolymer. The *SIS* process enhanced the etching contrast between alumina-containing PMMA domain and the polystyrene domain. Future work is focusing on the incorporation of electrocatalyst materials into the nanopatterned crevasses afforded from block copolymer templates. Note: All scanning electron microscope (SEM) images were taken with a FEI Quanta 3D FEG FIB/SEM.

Results and Discussion

Part 1: Understanding ionic domain connectivity and its relation to ionic conductivity

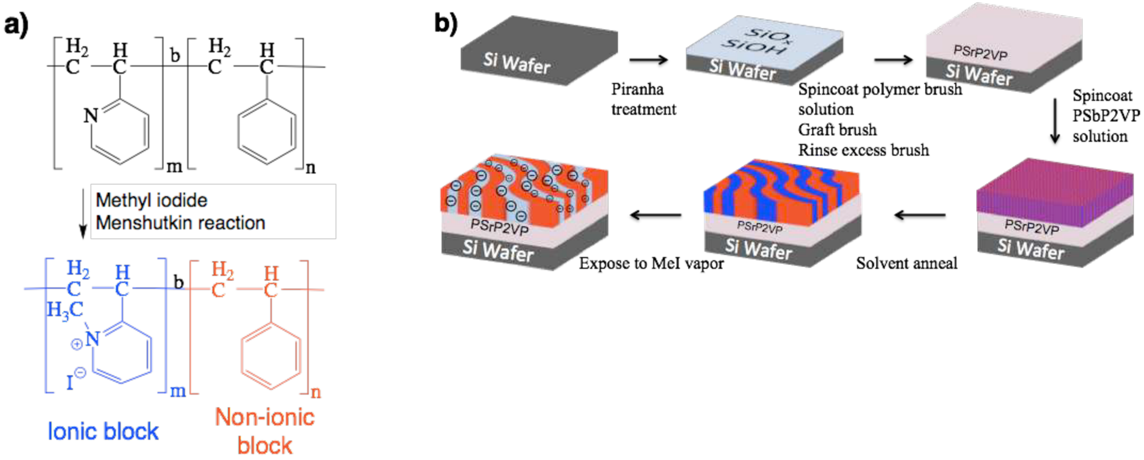

Figure 1. a.) Menshutkin reaction of PS*b*P2VP to poly(styrene-*block*-2-vinyl pyridine/n-methyl pyridinium iodide) (PS*b*P2VP/NMP$^+$ I$^-$). b.) Process flow diagram to make ordered BCE films. Images from reference (13).

Figure 1a depicts the Menshutkin reaction to prepare BCE films from PS*b*P2VP block copolymers. Figure 1b illustrates the process flow to make perpendicular aligned lamellae structures of anion conducting BCEs (PS*b*P2VP/NMP$^+$ I$^-$). The self-assembled block copolymer film exposed to methyl iodide vapor converted the non-conductive film into an ion conductor. Figures 2a and 2b give SEM images that were processed to highlight the degree of ion domain connectivity of self-assembled PS*b*P2VP/NMP$^+$ I$^-$ films (red color). The extent of ion domain connectivity (i.e., contiguous area fraction) was manipulated by altering the volume fraction of the P2VP block in the block copolymer system (18). Making the block copolymer system slightly more P2VP rich increased ion domain connectivity. Figure 3 is the ion conductivity (normalized per ion-exchange capacity) as a function of contiguous area fraction. A larger population of ion connected domains yielded a substantial improvement in ionic conductivity.

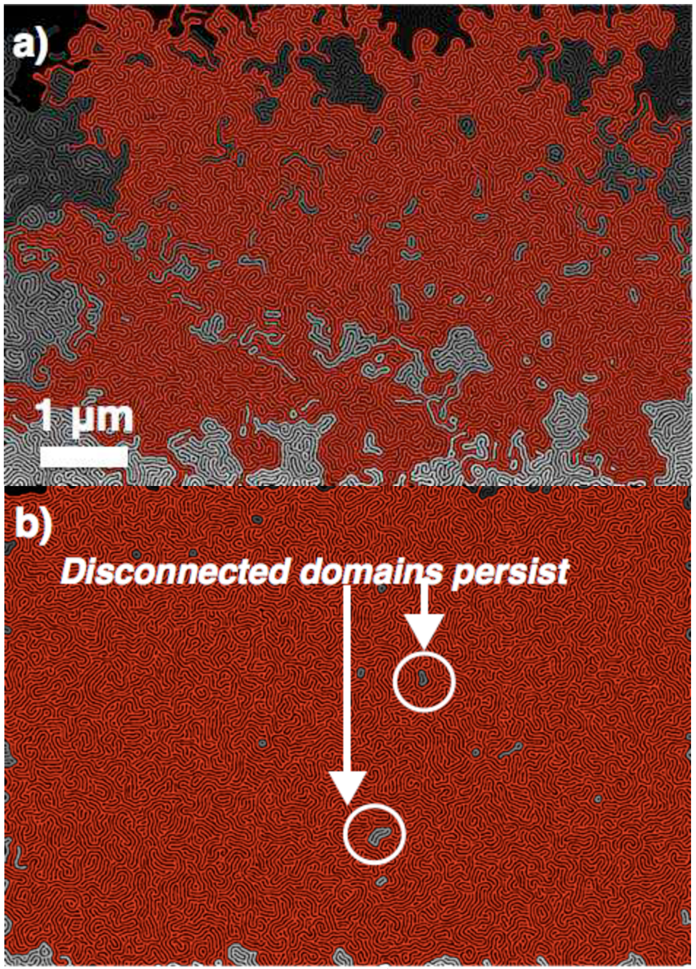

Figure 2. SEM images of a.) PS*b*P2VP/NMP$^+$ I$^-$ BCE film with a small population of interconnected ionic domains (represented by the red). b.) PS*b*P2VP/NMP$^+$ I$^-$ BCE film with a large population of interconnected ionic domains, but some disconnected domains still persisted. Images taken from reference (13).

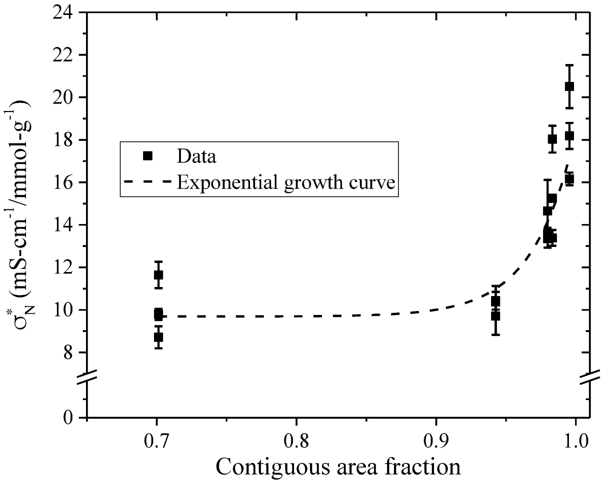

Figure 3. Normalized ionic conductivity to ion-exchange capacity for PS*b*P2VP/NMP$^+$ I$^-$ versus contiguous area fraction of interconnected ionic domains. Images taken from reference (13).

Part 2: Nanopatterns for electrocatalyst integration with glassy carbon and ion-exchange membranes

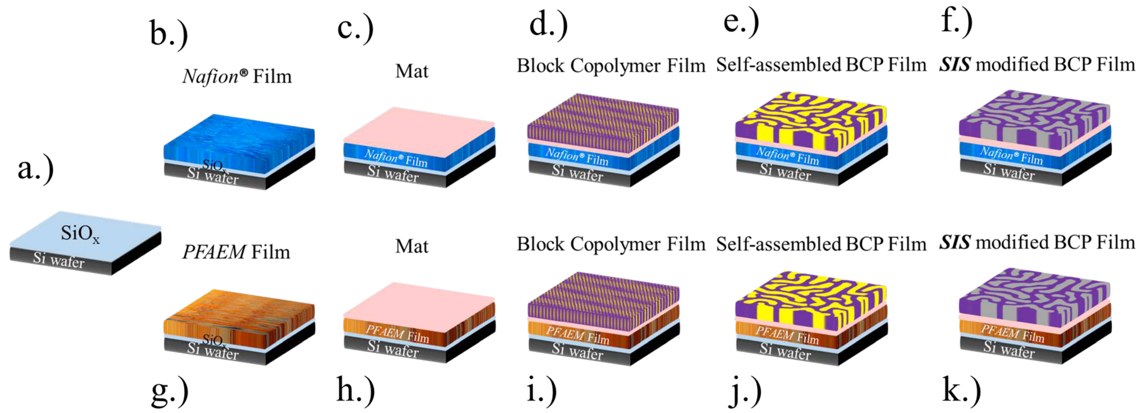

Figure 4. Process flow diagram of applying block copolymer lithography on the surface of ion exchange membranes. A similar procedure was applied to glassy carbon substrates. a.) bare surface of a silicon wafer; b.) dropcasted Nafion® membrane; c.) applied polymer mat with controlled surface energy on top of Nafion® membrane, thermally crosslinked the mat layer to prepare for block copolymer self-assembly; d.) spincoated block copolymer thin film on mat layer; e.) Thermally annealed block copolymer thin film to form self-assembled block copolymer patterns; f.) Perform *SIS* on the block copolymer thin film. Same procedure is repeated for PFAEM in steps g.) through k.).

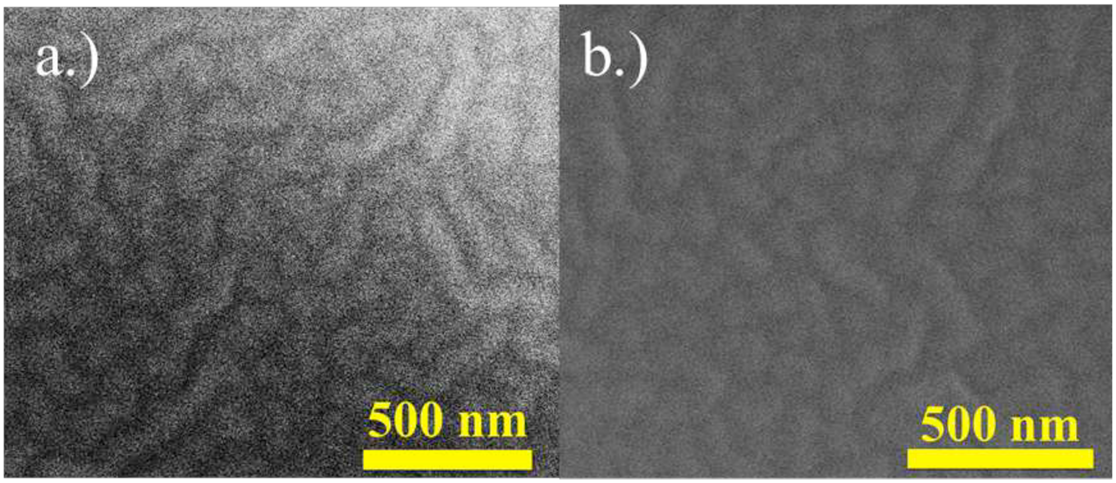

Figure 5. SEM images of block copolymer nanopatterns on a.) Nafion® membrane surface and b.) PFAEM membrane surface.

Figure 4 illustrates the procedure for applying block copolymer templates on top of ion-exchange membranes (e.g., Nafion® and PFAEM membranes) and glassy carbon substrates. The goal is to use those templates for the fabrication of periodic, nanoelectrocatalysts at the electrolyte or electron-conducting interface. Figure 5 provides SEM images of poly(styrene-*block*-methyl methacrylate/alumina) block copolymer structures on both Nafion® and PFAEM membranes. Figure 6 corresponds to lamellae- and cylinder-forming (PMMA rich) PS*b*PMMA block copolymers on glassy carbon substrates.

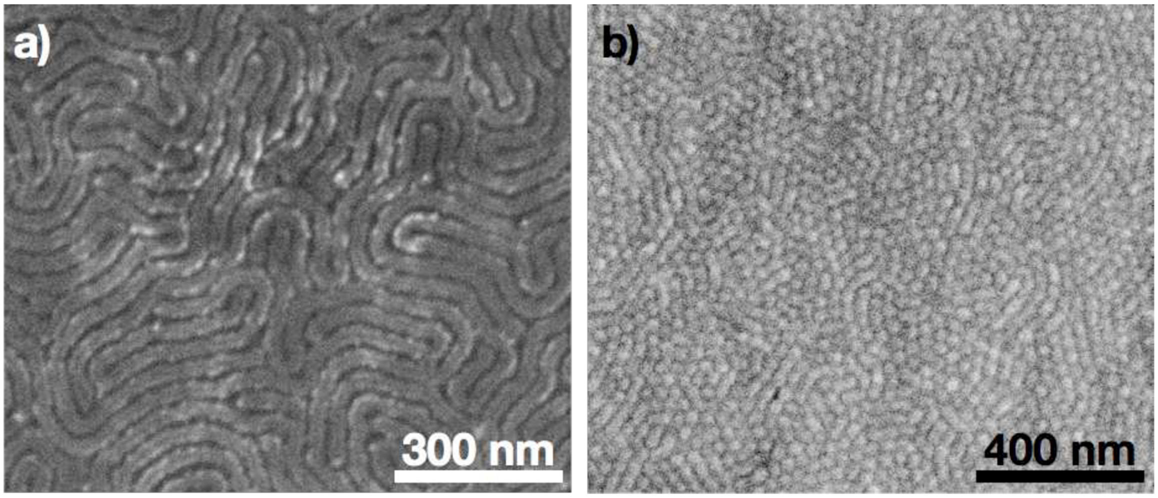

Figure 6. SEM images of block copolymer nanopatterns on glassy carbon substrates. a.) lamellae-forming PS*b*PMMA structure and b.) cylinder-forming (PMMA rich) PS*b*PMMA structure.

Conclusions

In this work, the utility of self-assembled block copolymers was illustrated for ion-conducting BCEs and patterning bulk ion-exchange membranes and glassy carbon substrates. The first part of the work revealed that greater populations of anion conducting channels in BCEs improved ionic conductivity by a factor of 2 to 3 over disconnected channels. The second part of the work demonstrated methods to place perpendicular aligned cylinders and lamellae structures on electrochemical materials like glassy carbon and ion-exchange membranes.

Acknowledgments

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