RESPONSE OF BLOCK COPOLYMER ELECTROLYTES TO IONIC CURRENT

Nitash P. Balsara[1,2]

[1]Department of Chemical and Biomolecular Engineering, University of California, Berkeley, California 94720, USA
[2]Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA

ABSTRACT

Lithium-salt-doped block copolymers have the potential to serve as solid electrolytes in rechargeable batteries with lithium metal anodes. In this work, we use small angle X-ray scattering (SAXS) to study the structure of polystyrene-block-poly(ethylene oxide) doped with bis-(trifluoromethylsulfonyl)amine lithium salt (LiTFSI) during dc polarization experiments in lithium-lithium symmetric cells. The block copolymer studied is nearly symmetric in composition, has a total molecular weight of 39 kg mol^{-1}, and it exhibits a lamellar morphology at all studied salt concentrations. When ionic current is passed through the electrolyte, a salt concentration gradient forms which induces a spatial gradient in the domain spacing, d. The dependence of d on distance from the positive electrode, x, was determined experimentally by scanning the incident X-ray beam from one lithium electrode to the other. By studying the 2D SAXS patterns as a function of azimuthal scattering angle, we find that lamellae with PS-PEO interfaces oriented perpendicular to the flow of ionic current swell and contract to a greater degree than those with interfaces oriented parallel to the current direction. While domains with the perpendicular lamellae do not provide direct conducting pathways between the electrodes, our analysis suggests they play an important role in establishing the salt concentration gradient necessary for sustaining large ionic current through greater expansion and contraction.

RESULTS AND DISCUSSION

There is considerable interest in the possible use of block copolymers in lithium batteries.[1-4] We studied a block copolymer which we call SEO(19-20) with added LiTFSI, the molar ratio of lithium ions to ether oxygens in the electrolyte was 0.16 [1]. This electrolyte was inserted in a custom electrochemical cell to allow simultaneous SAXS measurements. This cell is shown schematically in **Fig. 1a**. The lithium electrodes are in the y-z plane such that the nominal direction of ionic current is parallel to the x-axis. The length of the sample in the x-direction, L, was 0.14 cm. In **Fig. 1b**, we show an example of a SAXS pattern obtained from SEO(19-20) where the incident beam is oriented in the z-direction. By scanning the beam along the x-axis, the 2D scattering patterns contain information about the structure of lamellae with normal vectors in the x-y plane along the axis which the salt concentration gradient forms in a dc polarization experiment. We define the azimuthal angle, χ, in Fig. 1b and denote χ = 0° along the y-axis, pointing upwards and increasing counterclockwise. By analyzing data at χ = 0 and 180° (as defined in Fig. 3b) we obtain information about grains with PS-PEO interfaces oriented parallel to the flow of ionic current (we call these lamellae $\mathrm{LAM}_{||}$, and note that their normal vectors are parallel to the y-axis). For χ = 90 and 270°, we obtain information about grains with PS-PEO interfaces oriented perpendicular to the flow of ionic current (we call these lamellae $\mathrm{LAM}_{\perp}$, and note that their normal vectors are perpendicular to the y-axis).

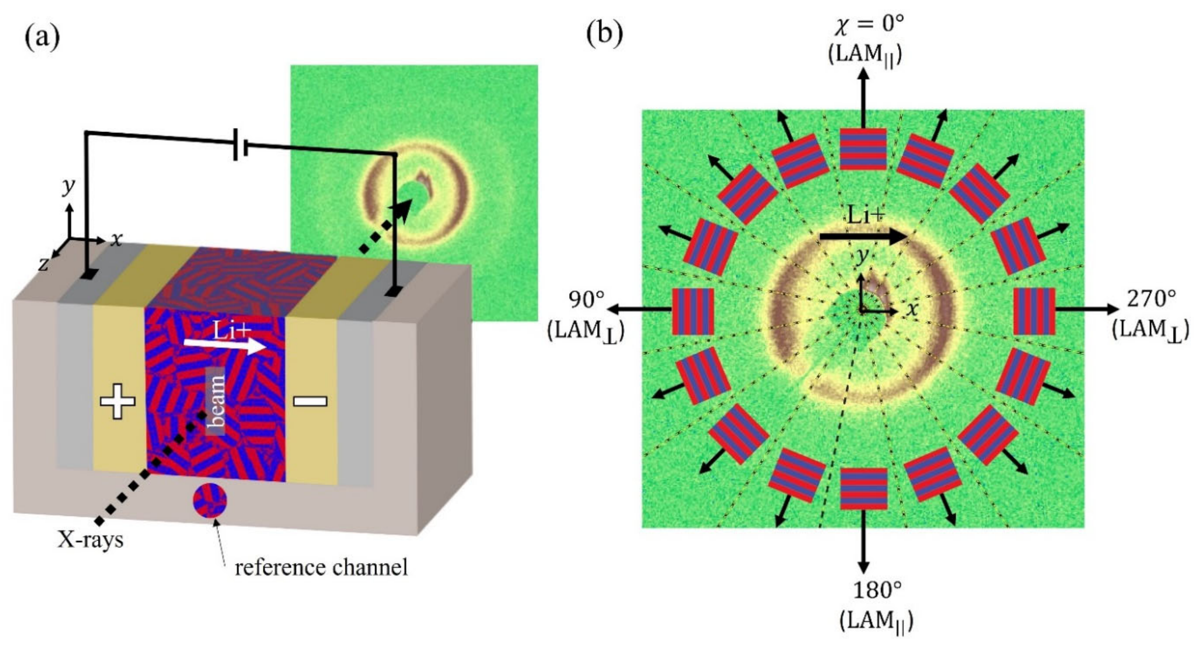

Figure 1: (a) Schematic representation of the simultaneous polarization and SAXS experiment. An SEO/LiTFSI electrolyte with randomly oriented grains is sandwiched between two lithium electrodes with current passing parallel to the x-axis. X-rays pass parallel to the z-axis, perpendicular to the current and the shaded gray box shows the beam footprint on the sample. Scanning the beam along the x-axis allows for spatial resolution between the electrodes. A reference channel filled with electrolyte was placed next to the electrochemical cell. (b) Characteristic 2D SAXS pattern obtained from experiments. The pattern is divided into 16 sectors defined by the azimuthal angle, χ. Scattering data in each sector corresponds to lamellae oriented with the angle between the vector normal to the PEO-PS interfaces and the positive y-axis equal to χ. The cartoons in each sector show the lamellar orientation with their respective normal vectors.

The SAXS data were used to determine the domain spacing, d, at three different current densities, i. We present data as a function of the normalized current density iL. Before polarization, we find that $d(\chi)$ was exactly not constant. To account for this, we redefine the quantity Δd for a fixed position x/L in Eqn. 16:

$$\Delta d(\chi, t) = d(\chi, t) - d(\chi, t = 0) \tag{1}$$

In **Figs. 2a-c**, we plot Δd as a function of χ for each position in the cell for the cells polarized at (a) iL = 1.96 µA cm^{-1} (b) iL = 3.74 µA cm^{-1}, and (c) iL = 11.1 µA cm^{-1}. The results presented in these figures show that grains with PS-PEO interfaces perpendicular to the flow of ionic current ($\text{LAM}_{⍰}$) undergo greater expansion (near the positive electrode) or contraction (near the negative electrode) when compared to those with PS-PEO interfaces oriented parallel to the flow of ionic current ($\text{LAM}_{||}$). To highlight this point, we plot the difference in lamella spacing between $\text{LAM}_{⍰}$ and $\text{LAM}_{||}$, $d_{\text{LAM}_{⍰}} - d_{\text{LAM}_{||}}$, in **Fig. 1d.** As the concentration gradient builds up, the $\text{LAM}_{⍰}$ near the positive electrode are swollen between 0.6 and 1.2 nm larger than $\text{LAM}_{||}$. Near the negative electrode, the $\text{LAM}_{⍰}$ are between 0.2 and 1.2 nm smaller than the $\text{LAM}_{||}$.

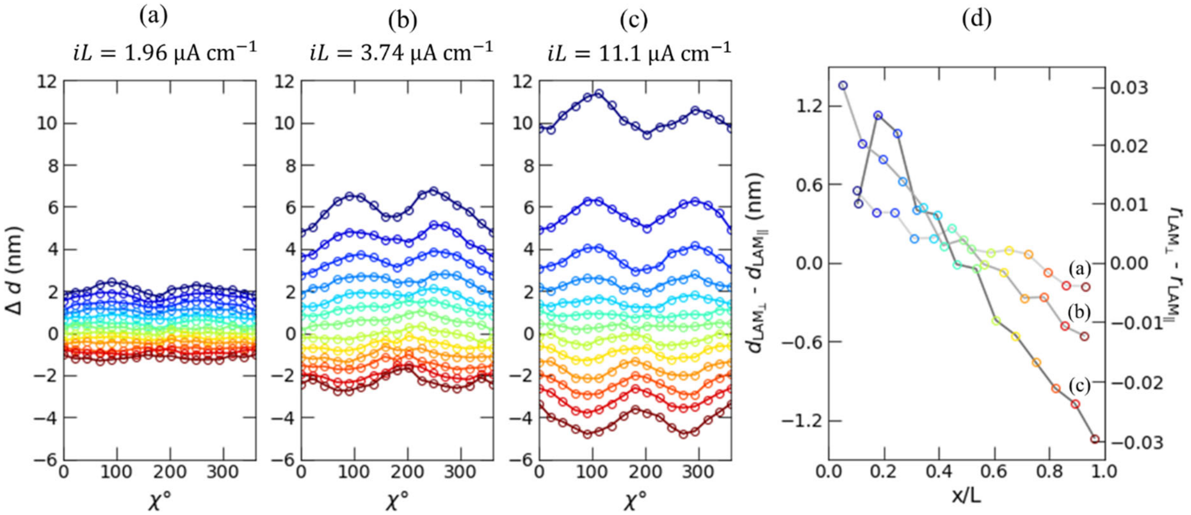

Figure 2: Orientation dependence of lamellar distortion. The change in domain spacing, Δd, defined by Eqn. 1 as a function of azimuthal angle, χ, is plotted for each cell position for the cell polarized at (a) iL = 1.96 μA cm^{-1} at t = 46.7 h, (b) iL = 3.74 μA cm^{-1} at t = 46.7 h, and (c) iL = 11.1 μA cm^{-1} at t = 60.7 h. Each data set is based on the last scan taken at the end of each polarization. (d) Difference in domain spacing between $\text{LAM}_\perp$ and $\text{LAM}_{||}$ as a function of normalized position, x/L, for the three data sets in (a), (b), and (c). The right axis is the difference in molar salt concentration, r, based on Eqn. 2. The color of each data set in (a), (b), and (c) correspond to the x/L position plotted in (d).

CONCLUSIONS

The SAXS experiments show that that there was a net increase in the domain spacing of the block copolymer as the salt concentration gradient develops. We observed that grains with PS-PEO interfaces oriented perpendicular to the flow of ionic current ($\text{LAM}_\perp$) swell and contract to a greater extent compared to those with PS-PEO interfaces oriented parallel to the flow of ionic current ($\text{LAM}_{||}$). It is obvious that $\text{LAM}_{||}$ play an important role in ion transport as the conducting domains in these grains are parallel to the direction of macroscopic ion transport. Our work indicates that $\text{LAM}_\perp$also play an important role. The formation of a salt concentration gradient that must arise due to ion transport across macroscopic length scales relies on the ability of the lamellae to swell and contract. These distortions occur to a greater extent in

$\mathrm{LAM}_{\perp}$. Both $\mathrm{LAM}_{||}$ and $\mathrm{LAM}_{\perp}$ appear to be necessary to accommodate large ionic currents in block copolymer electrolytes.

ACKNOWLEDGEMENTS

This work was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Vehicle Technologies Office, under the Advanced Battery Materials Research (BMR) Program, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

REFERENCES

1. Tu, Z.; Nath, P.; Lu, Y.; Tikekar, M. D.; Archer, L. A. Nanostructured Electrolytes for Stable Lithium Electrodeposition in Secondary Batteries. *Acc. Chem. Res.* **2015**, 48 (*11*), 2947–2956.
2. Newman, J.; Balsara, N. P. *Electrochemical Systems*, 4th ed.; Wiley, **2021**.
3. Cheng, X.-B.; Zhang, R.; Zhao, C.-Z.; Zhang, Q. Toward Safe Lithium Metal Anode in Rechargeable Batteries: A Review. *Chem. Rev.* **2017**, 117 (*15*), 10403–10473.Caenn, R.; Darley, H. C. H.; Gray, G. R. *Composition and Properties of Drilling and Completion Fluids*, 5th ed.; Gulf Publ Co, 1988.
4. Singh, M.; Odusanya, O.; Wilmes, G. M.; Eitouni, H. B.; Gomez, E. D.; Patel, A. J.; Chen, V. L.; Park, M. J.; Fragouli, P.; Iatrou, H.; Hadjichristidis, N.; Cookson, D.; Balsara, N. P. Effect of Molecular Weight on the Mechanical and Electrical Properties of Block Copolymer Electrolytes. *Macromolecules* **2007**, 40 (*13*), 4578-4585.