Looking at the Lag in Room-Temperature Ionic Liquids

Finding better energy storage technologies is a national priority that has led researchers to exotic substances such as room-temperature ionic liquids (RTILs). Such liquids consist of two molecules that have a positive and negative charge (as in table salt), but are unusual in that they remain liquid at room temperature. They have the potential to make excellent energy-dense batteries and supercapacitors, but their behavior at charged electrodes remains mysterious. For example, room-temperature ionic liquids are known to organize into separate layers of positive and negative charge where they touch a charged electrode, and these layers flip when the electrode’s potential changes from positive to negative or vice-versa. But the layers take a mysteriously long time to do so — up to 10 sec — an extremely long time for a molecular process. This lag leads to hysteresis, which means that the structure of the liquid’s surface at a certain electrical potential depends on how it got there; whether it started at a higher or lower potential as well as where it ended up.

Researchers are using the APS to get a better look at what happens on the molecular level in room-temperature ionic liquids to make their lag last so long. A better understanding of the phenomena could lead to more efficient, low-hysteresis designer liquids and superior energy storage devices.

Room-temperature ionic liquids have been known about for a long time, but they weren’t practical until the year 2000, when researchers discovered ones that were stable in air. Because every molecule in an RTIL can carry charge, such liquids could make energy storage devices that are much more energy dense than current technologies, in which most of the available space is taken up by the solvent the charge carriers flow through. Researchers have experimented with several different RTILs and electrode types and they always see the same thing. At the interface where the RTIL touches an electrode, the RTIL separates into layers of ions, with each layer either mostly positively or mostly negatively charged (Fig. 1). If the electrode has a positive potential, the RTIL will create a layer of mostly anions right against the electrode, with occasional patches of cations coexisting. If the potential of the electrode is then switched to negative, the ions will switch positions, with the ions adsorbed against the electrode gradually becoming mostly cations over a period of seconds.

Researchers from Vanderbilt University, Oak Ridge National Laboratory, Drexel University, and Argonne used the APS to get a more detailed understanding of how those layers of ions switch when the electrode potential changes. They used the XSD 6-ID-B, C, D, 12-ID-C, D, and 33-ID-D, E beamlines at the APS that use the high flux of high-energy x-ray photons to penetrate the RTIL and observe the evolution of the RTIL’s layered structure under electrochemical control and in real-time.

The researchers used a graphene electrode because it is thin and flexible and shows promise for many different applications. They had the graphene touch the surface of the RTIL 1-methyl-3-nonylimidazolium bis-(trifluoromethanesulfonyl)imide.

The measurements taken at the APS suggest the RTIL’s layered structure has two stable states—one when the electrode’s potential is positive, the other when the electrode potential is negative. The results suggest that these two stable states are separated by an energy barrier, which has a size of approximately 0.15 eV. This energy barrier is sufficiently large that it takes time (and energy) for the ions to cross over it, leading to the observed hysteresis. The team also noted intermediate states — mixed patches of anion and cations— while the potential applied to the graphene surface changed. The team members from Vanderbilt created a computer model that successfully reproduced those intermediate states, confirming that the researchers understood mathematically what is going on.

The next step will be to figure out what is happening in various RTILs. Specifically, the researchers want to know how the physical structure of the molecules in the RTIL contributes to the hysteresis. If the researchers can understand that, they can design RTILs with molecular properties that cause as little hysteresis as possible.

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Fig. 1. X-rays reflect off the interface between a room-temperature ionic liquid and a graphene electrode, revealing a layer of anions adsorbed onto the electrode. The layer flips charge when the electrode flips potential. Adapted from A. Uysal et al., J. Phys. Condens. Matter 27 032101 (2015). © 2015 IOP Publishing Ltd. All rights reserved

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