that do not represent a spin pairing or bond. In the selenium-containing radical, the corresponding Se--N interactions are stronger, evidently so much so that the diselenide bond of the σ-dimer cannot be induced to break at all using heat. In thiazyl radical 2 the inter-radical S--N interactions are weaker and by themselves may not provide the necessary energy barrier to realize hysteretic behaviour. Oakley and co-workers propose that these barriers do not represent a spin pairing or facilitate the formation of the corresponding Se∙∙∙N interactions are weaker. Perhaps the most obvious changes that accompany this transition are in the magnetic properties of the two phases, that is, diamagnetic at low temperatures and paramagnetic at high temperatures. As such the switching between spin states is in some ways reminiscent of the spin–crossover phenomenon in certain transition metal ions. As is the case for many interesting physicochemical properties, the unpredictability of non-covalent interactions, which seem to be important for the bistability in 1 and 2, poses some serious challenges for the rational design of radical-based hysteretic materials. Nonetheless, the dimerization of radicals, which was once thought to be the bane of chemists trying to make conducting or magnetic materials, is now proving to be quite an interesting feature in its own right.

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References

ELECTROCHEMICAL IMAGING

Waves in microscopy

Advances in transduction of electrochemical activity through surface plasmon resonance afford new opportunities for spatially and temporally resolved studies of interfaces.

Lane A. Baker and Chiao-Chen Chen

Tools for probing electrochemical processes at interfaces have proved crucial in investigating the chemical and biochemical nature of a number of complex systems. The workings of biological cells and tissues, catalytic materials, porous membranes and microfabricated structures often rely on electrochemical processes — electron transfer, capacitive charging or ion-concentration control, for example. Recently, spatially resolved studies have led to a deeper understanding of the nature of these processes.

Writing in Nature Chemistry, Tao and co-workers now describe1 a tool — electrochemical impedance microscopy (EIM) — that has enabled them to probe interfaces with high spatial resolution. The promise offered by EIM for the study of biochemical processes is demonstrated by a study of apoptosis (programmed cell death) and electroporation (the application of an external electric field that increases the conductivity and permeability of the cell wall).

Traditional electrochemical imaging relies on scanning probe techniques, in which electrodes are initially moved in close proximity to or in contact with the surface of the sample imaged. Raster-scanning the electrode over the sample — that is, collecting information at regular positions and then reconstructing the overall image — affords a method to spatially resolve electrochemical information collected at the tip of the scanning electrode (Fig. 1, left). Common forms of this type of imaging include scanning electrochemical microscopy, scanning ion-conductance microscopy and electrochemical atomic force microscopy2.

These scanning probe methods have significantly contributed to our understanding of reactivity, conductivity and kinetics at interfaces, but often have two shortcomings. First, probe fabrication can be tedious — or even impossible — when high-resolution imaging is required, particularly at the nanoscale. Second, the scanning nature of these tools can result in long image-acquisition times, on the order of minutes to tens of minutes depending on the area scanned and the resolution required. Probing the temporal response of electrochemical processes is often of interest, however, and lengthy scans can therefore present a major drawback as the processes of interest may occur on much faster timescales. Arrays of electrodes can be used to circumvent these issues to some extent, but high-resolution images are still difficult to obtain as the electrodes interfere with one another when they become too small. In the present approach, EIM overcomes these shortcomings by using light to measure electrochemical processes, eliminating the need for both raster-scanning and micro- or nanofabricated probes.

In plasmonic imaging, spatially resolved changes in the local dielectricity are transduced photонically through surface plasmon resonance (SPR)3. The sample to be imaged is placed on a transparent substrate coated with a thin layer of a metal, such as gold (Fig. 1, bottom right), and a laser is reflected from it. The wavelength of the incident laser is selected to match electronic oscillations (plasmons) in the metallic layer. As the incident beam creates surface plasmon waves in the layer, local changes in the dielectric constant near the metal surface can then be measured as shifts in the resonance frequency, in the resonance angle or in the absorption of the photons reflected.

Imaging by SPR has proved to be an extremely versatile tool — it is now commonly used to measure the kinetics and
binding constants of biological complexes. In recent work by Tao and others, in addition to its role as a plasmonic interface, the thin metallic layer also serves as the working electrode of an electrochemical cell. The ability to control the potential of the thin metallic layer relative to an external electrode, placed in the solution surrounding the sample image, enables the electrochemical processes to be driven. When these electrochemical processes affect the local dielectric constant, the signal can be transduced through changes in surface plasmon resonance, and subsequently collected and converted into electrochemical images.

In the present EIM approach, plasmonic imaging of electrochemical processes has been extended to electrochemical impedance — a measure of the resistive and capacitive components of a sample. In Tao and co-workers’ approach, the electrochemical response of the interface between sample and metal is recorded by applying an oscillating potential difference to the thin metallic layer. Local changes in impedance, induced by local changes in polarizability and conductivity at the interface, affect the SPR, which can be measured. The only requirement for impedance measurements is that they are carried out in an ionic solution — that is, no redox mediator is needed. This makes EIM particularly promising for biological samples where redox mediators may perturb the system being studied.

To demonstrate the utility of EIM, cellular samples (human cervical cells) were subjected to apoptosis and electroporation — both techniques that involve large changes in local polarizability of the cells. In each case, heterogeneous changes in cellular features were observed by simultaneously recording three types of images: conventional optical and SPR images, as well as impedance images through EIM. Images were obtained with a spatial resolution on the order of 3 µm, temporal resolution of 380 frames per second, and low detection limits for the impedance (2±PS). Compared with the conventional SPR and optical images, the impedance images seem to have higher contrast, and also contain additional information on the cellular structure. This was especially true for the electroporated samples: significant transient changes were observed for EIM images during the electroporation process, whereas optical and SPR images showed little difference in contrast. Aspects of EIM were interpreted with the aid of numerical simulations that modelled cells in a polarizable medium.

The future of electrochemical imaging via EIM and related measurements of electrochemical processes using plasmonic microscopy is exciting. The instrumental requirements — lasers, charge-coupled devices, function generators — are already commonly used in advanced optical microscopy, and it should be relatively easy to incorporate these tools with existing imaging techniques. Of course, there is room for improvement to expand the use of impedance microscopy. Better spatial and temporal resolution could be achieved through hardware development (for example tuning the excitation wavelength and frame rate), and a more thorough theoretical model would help in the collection of more quantitative results.

Impedance tools are also not currently compatible with every sample: the fact that a plasmonic active surface is required means that insulating materials may prove difficult to interrogate. Furthermore, any topographic information gained with scanned probe techniques (and so recorded from vertical displacements of the scanned probe) is lost. It would also be helpful to compare EIM to other existing characterization methods, for example by looking at reversible changes in the conductivity of an ion channel. Finally, it would also be valuable to image sample impedance as a function of excitation frequency to record a more complete electrochemical response — the frequency component of impedance is one of the most common ways to measure impedance, so usually the frequency is scanned.

Plasmonic microscopies might also exploit other methods of electrochemical measurement. Beyond biological samples, EIM could find wide application in conductivity measurements, especially in the realm of energy and materials science in which local charge densities play pivotal roles. In any case, this microscopy approach shines a new light on interfacial electrochemistry, and promises new routes for studying conductivity on small scales.

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