Scanning Electrochemical Microscopy: A local view of electrochemistry

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Abstract
The use of scanning probe electrochemistry techniques is growing, and has reached traditional fields from batteries to biology, and even some unexpected ones like fine art, forensics, and meteorites. This branch of scanning probe microscopy is an exciting way to correlate local features with the electrochemical properties of a sample, allowing local insight into a sample not possible otherwise. While the field of scanning probe electrochemistry encompasses a number of different techniques which provide complementary information on everything from sample topography to activity, this article will focus on Scanning ElectroChemical Microscopy (SECM), which is by far the most popular technique in this field. SECM is a chemically selective microscopy which measures the interaction of a sample with a mediator in solution using a probe in close proximity to the sample. Using SECM it is possible to locally investigate sample activity, conductivity, and topography. It is well suited to studies in biology, novel materials, corrosion, and catalysis, amongst others.

Introduction
Discussion of scanning probe microscopy techniques available to researchers is often limited to atomic force microscopy and scanning tunneling microscopy. By limiting these discussions, a growing field of techniques which can provide insight on everything from surface topography, to activity, to information about the work function of a sample is ignored. This is the field of scanning probe electrochemistry - a class of scanning probe microscopy which primarily investigates the local electrochemical nature of a sample. Scanning probe electrochemistry is the intersection of bulk electrochemistry and local microscopy measurements. Bulk electrochemical measurements are an averaged global view of the sample of interest which do not present a clear picture of the processes occurring at the sample. Microscopy measurements, on the other hand, provide information about the local features of a sample, but do not provide insight on the role these features play in the electrochemical processes occurring at the sample. Scanning probe electrochemistry combines these two fields, to provide a localized view of the electrochemical processes. The wide variety of sample characteristics measured with scanning probe electrochemistry is illustrated in Figure 1. The most popular technique in the scanning probe electrochemistry family is Scanning ElectroChemical Microscopy (SECM), which was introduced in 1989 by A. J. Bard (Bard et al. 1989). Since its introduction subsequent improvements on the initial SECM experiment have allowed it to be applied to a wide variety of fields. SECM utilises an ultramicroelectrode probe in close proximity to the sample. The probe is electrically biased to measure a redox mediator in solution, whose interaction with the sample is of interest. In this way the SECM probe can be raster scanned across a sample to measure its activity with respect to the redox mediator; Figure 2. As a result, SECM has an inherent chemical selectivity. SECM can be applied to any field in which bulk electrochemistry is used. For example, it has been used extensively in corrosion and coatings studies. SECM has been used in materials characterisation, including novel alloys and 2D materials. Using SECM, it has also been possible to investigate green energy materials, such as those used in batteries, photovoltaics, and fuel cells. Outside of fields traditionally considered when looking at electrochemistry, SECM has also been used in the study of biological systems, such as living cells, and biosensors. It has even been used in arts studies analysing the pigments used in paints (Doméch-Carbó et al. 2015).

History of SECM
SECM was introduced shortly after the introduction of atomic force microscopy. The basis of the SECM technique rests in work done by Royce Engstrom in 1986, which utilised an ultramicroelectrode (for SECM this is an active diameter of 25 μm or less) held in close proximity to a macroelectrode (in this study a diameter of 1 mm) (Engstrom et al. 1986). With the ultramicroelectrode held within the diffusion layer of the electrochemically biased macroelectrode it was possible to measure chemical species as they diffused from the macroelectrode to the ultramicroelectrode, which was also biased. Exploiting the resulting measured Faradaic current allowed the concentration of the chemical species to be spatially resolved. Three years later in 1989, SECM in its current form was introduced by A. J. Bard in the first of a series of publications describing its theory and use (Bard et al. 1989).

In this initial publication it was demonstrated that the ultramicroelectrode could be used to measure Faradaic current resulting from the diffusion of a chemical species between the ultramicroelectrode probe and even an unbiased sample. The result was a technique capable of spatially resolving the electrochemical activity of a conductive or non-conductive sample which did not need to be biased, or even electrically connected, for the measurement. Furthermore, the current measured by the probe was demonstrated to be related to the distance to the sample, with increased current magnitude arising from reduced probe-to-conductor distance, and decreased current magnitude arising from reduced probe-to-insulator distance, reflecting topography. SECM was therefore proposed as a technique to measure topography, sample activity, and electrochemical analysis and microfabrication. From here SECM was quickly applied to the study of biological samples (Lee et al. 1990), membranes (Scott et al. 1991), and corrosion samples (Wipf 1994) to name only a few.

Although SECM was initially used exclusively in the direct current mode (dc-SECM) as introduced by
of liquids, from low conductivity liquids such as tap water to high conductivity liquids like sea water analogue, to fully reflect the real-life environment of the sample. Importantly this also removes the possibility of adverse side effects from the use of a redox mediator like cell death. In ac-SECM the sample impedance is measured, which can offer a direct reflection of the sample conductivity. As with dc-SECM it is also possible to measure the sample topography using ac-SECM.

When SECM was first introduced it was as a constant height technique only. However, with many scanning probe microscopies it has been adapted to allow constant distance measurements to maintain the probe-to-sample distance throughout the measurement. In SECM this can be particularly beneficial because it removes the influence of topography on the sample activity signal, Figure 3. Constant height measurements have been achieved through the use of both electrical and mechanical feedback. The probe-to-sample distance can be maintained in SECM by electrical feedback in the constant current technique. In this technique the probe is controlled to the sample surface through the use of a set point current due to the Faradaic current of the redox mediator in solution (Lee 2002). To work effectively, constant current SECM requires that the sample activity is homogeneous with respect to the redox mediator of interest and that the bulk current does not decay throughout the measurement, which limits its applicability. More often a mechanical control is used in constant distance SECM experiments. There are a number of approaches to achieve this. Shear force SECM was one of the first methods of this kind, introduced in 1995 (Ludwig et al. 1995). In this technique the probe vibrates laterally, with the shear forces of the sample affecting the probe vibration. Changes in the probe vibration are monitored to maintain a similar probe vibration. Like shear force SECM, Intermittent Contact (ic)-SECM also uses probe vibration to maintain a set probe-to-sample distance (McKelvey 2010). In this case, however, the probe is vibrated perpendicular to the sample, with the interaction with the sample surface resulting in a change to the resulting vibration. Again, this change in vibration is accurately measured and used to control the probe to the sample surface. Both of these techniques allow simultaneous imaging of sample topography and activity. Another approach to constant distance SECM is to combine this technique with Atomic Force Microscopy (AFM) in SECM-AFM, which was first introduced as a technique to simultaneously measure sample activity and topography in 1999 (Jones et al. 1999). In this technique the AFM probe has a built-in ultramicroelectrode, although this probe is not the typical flat disc shape optimised for SECM measurements. Finally, soft stylus probes have been developed for constant distance SECM (Cortés-Salazar 2009). In this solution the probe is brought into contact with the sample and moved over it like a paint brush, allowing the measurement of sample activity without the influence of topography, although topography is not measured. These constant distance techniques have allowed the expansion of SECM to samples whose topography would have once ruled SECM out as an option for analysis.

Advancement of the SECM technique is still ongoing, with a recent review citing that almost 20% of publications focused on instrument development (Polcarí et al. 2016). Recent trends have included the combination of SECM with other techniques, as well as the development of related techniques such as scanning electrochemical cell microscopy (Kleijn et al. 2012). As with other scanning probe microscopies the probe is key to the success of the SECM technique, with the probe determining the ultimate signal measured. As a result, probe development has also been ongoing. In SECM the probe controls the resolution of the measurement, with smaller probes allowing higher resolution measurements. Due to this, efforts have been made to reduce the probe size, with the setup required to reliably produce nanoscale SECM measurements recently reported (Kim et al. 2016). The active material of the probe is also important, as this determines how the probe interacts with the redox mediator. Platinum is by far the most popular material used, though a number of other active materials are also used (Danis et al. 2015).

**How dc-SECM works**

dc-SECM is still the most popular form of SECM and is typically the version researchers refer to. In this mode a dc bias is applied to the ultramicroelectrode probe in close proximity with the sample of interest to measure the Faradaic current of a redox mediator. The interaction of the redox mediator with the sample affects the current measured by the probe, reflecting the relative electrochemical activity of the sample in the area directly under the probe. In this way it is possible to build up a map of local sample activity with chemoselectivity. Typically, dc-SECM measurements are performed in what is called feedback mode. In feedback mode a three-electrode cell is formed between the SECM probe, and a separate reference and counter electrode. The SECM probe is biased to reduce (oxidise) the redox mediator in solution. The sample of interest is submerged in solution, but crucially it is not connected as an electrode, nor does it need to be a conductive material. When the probe is over a conductive region, or more specifically a region active towards the redox mediator, decreasing the probe-to-sample distance causes an increase in the current magnitude measured by the probe compared to the initial bulk measurement. This is referred to as positive feedback and occurs because the active region acts to return the mediator to its original state to further interact with the probe. On the other hand, when the probe-to-sample distance is reduced over an insulating, or electrochemically inactive, region the current magnitude measured by the probe decreases compared to the initial bulk measurement. This is referred to as negative feedback. In respect to the negative feedback measured it is important to note the construction of the SECM probe. The SECM probe is an ultramicroelectrode surrounded by an insulating
glass sheath. The glass sheath is typically a cone shape at the end to strictly control the ratio of the active to insulating electrode. Negative feedback is due to the diffusion of the redox mediator to the active region probe being blocked by the insulating sheath of the probe. When SECM is performed in feedback mode, therefore, two different types of contrast can be seen in any image. The first type of contrast is the change in current due to sample activity. In a sample with heterogeneous activity the probe will detect the highest current over the most active regions, and the lowest current over the least active regions. The other type of contrast measured by feedback mode SECM is due to topography. When a homogeneously insulating sample with varying surface topography is measured in feedback mode, SECM regions with the highest topography will be reflected by the lowest measured current, while regions with the lowest topography will have the highest measured current. The result is that feedback mode SECM can be used to measure both the activity and topography of a sample. It is also possible to make electrical connection to the sample to allow it to be biased during measurement in generator collector mode, and competition mode. An in-depth discussion of these two modes is outside the scope of this article. Briefly in the competition mode, SECM can be used to measure both the probe and the sample to allow feedback, generator-collector, and competition mode experiments to be run. The control electronics interface between the scanning system, potentiostat, and control PC to run the SECM experiments. If ac-SECM is to be performed a frequency response analyser is typically included. For constant distance measurements further hardware may also be included.

Advantages of SECM

SECM offers a number of unique advantages over other techniques. This includes the chemical selectivity of the technique, the ability to perform measurements in situ, the fact that it is a non-contact, non-destructive measurement, and its ability to measure samples without electrical connection. These advantages will be outlined using a number of examples.

The inherent requirement of dc-SECM for a redox mediator to be present in solution means it has an in-built chemical selectivity. Using dc-SECM it is possible to investigate the interaction of a sample with different species, or to produce a species, in the form of a redox mediator. The chemical selectivity of SECM has been exploited in investigations of ion diffusion through membranes (Scott et al. 1991), the lithiation and delithiation of battery electrodes (Xu et al. 2011), and for catalysis studies, for example in the investigation of the affinity of the Pt-H bond (Papaderakis et al. 2017). The usefulness of this chemical selectivity can be demonstrated by the use of oxygen as the redox mediator of interest, which has been utilised in a number of areas. The direct interaction of the sample with oxygen is of particular interest for studies of electrocatalytic oxygen reduction reaction. By generating oxygen at the SECM probe, and measuring its use in oxygen reduction at the sample it is possible to determine the local electrocatalytic activity of a sample and screen different materials (Lu et al. 2007). This chemical selectivity has also been exploited in corrosion studies. Oxygen is used during cathodic corrosion of a metal sample in solution. When the SECM probe is biased to perform oxygen reduction, the probe and the sample both compete for the oxygen dissolved in solution. In regions with high rates of corrosion, a lower current will be measured by the probe than in regions with low rates of corrosion (González-García et al. 2011). In this way it is possible to use the chemical selectivity of oxygen in an SECM experiment to map local corrosion. As a final example the chemical selectivity of the SECM technique has been used in biology. During photosynthesis oxygen is released from the stomata of plant leaves. By biasing the SECM probe to drive oxygen reduction it is possible to measure the oxygen production during photosynthesis and map the location of stomata on the leaf, Figure 6.

It is also an integral requirement of SECM that the measurement is performed in solution, unlike other scanning probe microscopies. This has the distinct advantage that measurements can easily be performed in situ. Of great interest in the improvement of battery systems is an understanding of the formation of the Solid Electrolyte Interface (SEI). As the SEI forms the electrochemical activity of the battery electrode changes. SECM is therefore an ideal technique to follow SEI formation in situ. This is particularly beneficial because SECM allows the battery electrode to be measured at different stages of cycling to determine its effect on the SEI (Liu et al. 2019). It is also important to study super capacitor electrodes in situ. By performing in situ SECM approach curve measurements of super capacitor electrodes, it has been possible to investigate the swelling of the electrodes during cycling, allowing the interaction of the electrode with the electrolyte to be understood (Fic 2019). When investigating corrosion processes it is also important to perform measurements in situ. For example, using SECM it has been possible to investigate the effects of different salts in seawater on magnesium using in situ measurements (Cao et al. 2019). A further example of SECM measurements being performed in situ is demonstrated in Figure 7, which shows an intermittent contact ac-SECM measurement scratch in a drink can measured in situ.
SECM is a non-contact, non-destructive measurement. It can be performed at further probe-to-sample distances than other scanning probe microscopies. This is particularly advantageous for soft biological samples which could be detrimentally affected by contact. Due to this non-contact nature of the SECM measurement, it has been used to measure the morphology of live cells with good correlation to optical microscopy, and the added advantage that the 3D morphology can be determined. This is useful because it allows the influence of external stimuli on 3D cell morphology to be accurately determined without the influence of the probe (Razzaghi et al. 2015). SECM affords these sorts of measurements a further advantage due to its inherent chemical selectivity, which means that unlike many other microscope measurements, SECM is a label-free measurement.

SECM can be applied to measure sample types ranging from fully conducting, to completely insulating samples. Therefore, samples can be measured without the need for electrical connection. This opens SECM measurements up to samples which would otherwise be off limits. Because sample contact is not necessary, SECM studies of 2D materials allow measurement of the material of interest without sample preparation (Henrotte et al. 2017). SECM has therefore been used to perform local conductivity studies of graphene oxide, showing similar results to those obtained from the bulk conductivity technique of four-point probe measurements (Azevedo et al. 2013). In the investigation of sensors, it has been possible to measure patterned arrays of horseradish peroxidase on glass substrates, without electrical contact to the array (Roberts et al. 2011). These SECM measurements allowed the activity of the enzyme arrays to be analysed, which would not be possible otherwise.

**Conclusion**

SECM is the most popular technique in the field of scanning probe electrochemistry. Using SECM it is possible to locally investigate the activity, conductivity and topography of a sample. SECM has a number of unique advantages. Of particular interest in a number of applications is the inherent chemical selectivity of the SECM technique. Also important is its ability to measure local electrochemistry in situ, providing an in-depth view of processes as they occur. The unique advantages of SECM mean it has been applied in fields as varied as biology and batteries. Its inclusion in the scanning probe microscopy toolkit provides researchers the ability to understand sample characteristics which would otherwise be off limits.

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Samantha is the Product Manager for scanning probe electrochemistry products at Bio-Logic Science Instruments. This role exposes her to the latest technological developments in scanning probe electrochemistry. Furthermore, this provides her with exposure to the growing range of application areas to which scanning probe electrochemistry is used. Samantha gained her PhD from the University of Liverpool in 2014. During her PhD she focused on the field of single molecule electronics and spintronic systems in ionic liquids. These systems were studied using bulk electrochemistry and electrochemical scanning tunnelling microscopy.

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