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Review Article Redox cycling in nanogap electrochemical cells Henry S. White¹ and Kim McKelvey^{1,2,*}



The repeated oxidation and reduction of a redox species (redox cycling) in a gap between two working electrodes has primarily been used to study the kinetics of electrochemical reactions. New fabrication methods have allowed the gap between the two working electrodes to be reduced to 10's of nanometers in size. This reduced nanogap width has allowed recent innovations such as single molecule electrochemistry and probing the effect of electrical double layer on molecular transport at electrode/electrolyte interfaces.

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Introduction

A nanogap electrochemical cell is created by precisely separating two working electrodes by a 10-100 nm wide layer of electrolyte, as depicted in Figure 1. The potential of each electrode is controlled independently with respect to a reference electrode in the bulk solution (i.e., outside the nanogap) and the current at each electrode measured separately. Typically nanogap electrochemical cells are operated in a generation/collection configuration [1], where one electrode is held at an oxidizing potential and the second electrode at a reducing potential, allowing a redox species to be oxidized at one electrode, transported across the nanoscale gap between the electrodes (by a combination of diffusion, migration and convection) and then be reduced at the second electrode. The nanogap traps the redox species and allows the redox species to repeatedly cycle between the two electrodes, which leads to a greatly enhanced electrochemical signal, a process called redox cycling (or positive feedback in the scanning electrochemical microscopy literature) [2].

The idea of redox cycling in a gap between two working electrodes was developed 50 years ago as twin-electrode thin-layer electrochemistry by Reilley and coworkers [3,4^{••}], based on the earlier work on thin-layer electrochemistry [5]. This early work focused on micrometer scale gaps between electrodes and measuring the kinetics of electrochemical reactions. Recent developments in device fabrication, either using nanolithographic methods or scanning electrochemical microscopy techniques, have allowed creation of gaps on the length scale of 10's of nanometers. The development of the nanogap electrochemical cell has provided a means to investigate single molecule electrochemistry and the effect of the double layer on molecular transport at charged interfaces. A nanogap electrochemical cell also provides an interesting configuration for electroanalytical sensing applications due to the very high signal amplification that is generated by redox cycling, an aspect not covered here but discussed in detail elsewhere [6].

Nanogap fabrication

Fabrication of nanogap electrochemical cells is challenging, especially for nanogaps with widths less than 100 nm due to imperfections in the fabrication process leading to contact and shorting between the two electrodes. The two main methods of fabrication include either using photolithographic methods to define the two closely spaced electrodes [7] or using a scanning electrochemical microscope to bring two electrodes close together [2].

Photolithographic methods rely on the patterned deposition thin films of electrode material onto a substrate. The first electrode is deposited on a planar substrate, followed by a sacrificial separator layer and then by the second electrode to give structures like is shown in Figure 2A [8^{••}]. The sacrificial layer is removed, typically by electrochemical etching, leaving the two working electrodes separated by a nanogap that can be subsequently filled with solution. Different nanogap widths can be created simply by altering the thickness of the sacrificial layer. Recently reported variations of the photolithographic fabrication procedure include work by Bohn and coworkers in which an array of nanopores is created in a photolithographic defined electrode-separator-electrode stack by focused ion beam [9] or by reactive ion etching to create an array of ring-disk electrodes as is shown in Figure 2B [10[•]]. Simpler fabrication processes can be used to create 2D and 3D





Diagram of redox cycling in a nanogap electrochemical cell with two working electrodes separated by a thin layer of electrolyte and a reference/counter electrode in the bulk of solution.

interdigitated electrode arrays [11–13] or nanogap transducers [14,15] which allow redox cycling between two working electrodes arranged on a planar surface but with a reduced cycling efficiency as redox species are not fully confined within a nanogap and therefore can diffuse away from the electrodes into the bulk of the solution.

The second popular method to create a nanogap between two working electrodes is to use scanning electrochemical microscopy to position a small electrode close to a second larger electrode, as shown in Figure 2C [16^{••}]. The scanning electrochemical microscopy method allows nanogap size to be controlled simply by moving the two electrodes closer or further apart. In addition, the ability to deconstruct the nanogap and clean the electrode surfaces can be advantageous.

Single molecule electrochemistry

Measuring the electrochemical response from a single molecule requires that there be only one molecule present in the nanogap cell volume. This can be achieved by reducing the concentration of redox species or by reducing the nanogap volume. This approach was originally demonstrated by Fan and Bard [17^{••}], and Sun and Mirkin [18] using a nanogap created using a scanning electrochemical microscopy approach.

In recent work Lemay and coworkers have continued to pioneer single molecule measurements in photolithographically defined nanogap cells, as shown in Figure 3A [19,20,21°,22,23°]. The two current traces (one for the oxidation current on one electrode and one for the reduction current on the other electrode) in Figure 3A for the ferrocenylmethyltrimethylammonium (FcTMA^{+/2+}) redox couple are measured concurrently and show the redox cycling of single molecules in the nanogap. The current– time trace in Figure 3A shows four single molecules entering the nanogap electrochemical cell over the 120 s time frame, with each resulting in an increase in magnitude of both the oxidation and reduction currents which return to baseline when the molecule exits the nanogap.

Single molecule electrochemistry has also been recently demonstrated using a variation of the scanning electrochemical microscopy type nanogap [24]. In this case, nanogap electrochemical cell was created in a small drop of solution at the end of a multichannel probe that incorporated a working electrode and two open channels, as



A. Lithographically fabricated nanogap electrochemical cell. Top showing an optical image of the two Pt working electrodes and the sacrificial Cr layer, and below a diagram of the final cell geometry. (Reproduced with modification from [8].) B. An array of ring-disk nanogap cells fabricated using lithographically defined electrodes and reactive ion etching. (Reproduced with modification from [10].) C. A nanogap created between the end of a planar disk-shaped microscale electrode and a larger electrode surface. (Reproduced with modification from [16].)





A. Single molecule electrochemistry of FcTMA^{+/2+} in a 0.1 M KCl aqueous solution in a lithographically defined Pt-electrode nanogap electrochemical cell. (Reproduced with modification from [23].) B. Single molecule electrochemistry of FcTMA^{+/2+} in [BMIM][BF4] in a scanning probe configuration between carbon electrodes in the probe and a Pt substrate electrode. (Reproduced with modification from [24].)

is shown in Figure 3B. The multichannel probe configuration enables the width of the nanogap to be controlled by moving the probe vertically, and restricts the contact area between solution and the electrodes and so enabling both the oxidation and reduction currents to be measured with very low background noise levels of 2 fA. Typical traces showing single molecule electrochemistry in this configuration for the FcTMA^{+/2+} redox couple are shown in Figure 3B.

Bohn and coworkers have reported recent work which used arrays of nanogap sensors to isolate single molecules, with an average of less than one molecule in each nanogap in the array [25]. Although the current measurement is averaged over the entire array of nanogap electrodes, and therefore the signal from a single molecule cannot be viewed in isolation, this configuration has the potential to couple secondary detection methods with single molecule electrochemical methods.

The theoretical diffusion limited current for a single molecule in a nanogap, assuming the nanogap is much longer than it is wide, is $i_{redox} = eD/z^2$ [17], where *e* is the charge on an electron, *D* is the diffusion coefficient and *z* is the nanogap width. In a 40 nm wide nanogap a single molecule of FcTMA^{+/2+} (which has a diffusion coefficient of 6×10^{-6} cm² s⁻¹) would be expected to generate a current of 60 fA. However, as shown in Figure 3A the experimentally measured current of a single molecule of FcTMA^{+/2+} in a 40 nm nanogap is only ca., 10 fA. The discrepancy between the theoretical and measured diffusion limited currents has been attributed to the absorption

of the outer sphere redox species to the electrode surface [26], which results in the reduction of cycling efficiency and reduction the magnitude of the measured current.

Single molecule electrochemical measurements have proved to be experimentally challenging, requiring very low noise configurations and precisely defined nanogap cells. In addition, interpreting the inherently stochastic data (most obviously in the Brownian motion of the molecule [27] but also in the probabilistic absorption of the molecule to the electrode surface) is not straight forward as it requires averaging together the response of many single molecules. Looking forward single molecule electrochemistry needs to expand beyond simple outer sphere redox species (typically ferrocene derivatives) that have been popular so far.

Redox cycling with double layer effects

The second recent innovative use of nanogap electrochemical cells is to probe electrical double layers. Using a nanogap electrochemical cell to trap a redox species in a region that is on the same scale as the electrical double layer provides a simple and effective method to probe the electrical double layer. The nanogap width and the electrical double layer size can be made commensurate by either reducing the width of the nanogap or by working in a low ionic strength solution. In fact even when the electrical double layer does not span the entire nanogap the effect of the double layer on the redox cycling can be significant, for example a double layer effect is still observed at 10 mM [TBAPF₆] supporting electrolyte in the



A. Oxidation current for the cyclic voltammetry for the FcTMA^{+/2+} redox couple in a 210 nm nanogap cell as a function of supporting electrolyte concentration. (Reproduced with modification from [29].) B. Reduction current for the cyclic voltammetry of the $Ru(NH_3)_6^{2+/3+}$ redox couple in a 147 nm nanogap as a function of supporting electrolyte concentration. (Reproduced with modification from [8].) C. Cyclic voltammetry for the $Ru(NH_3)_6^{2+/3+}$ redox couple in a nano ring-disk array as a function of supporting electrolyte strength. (Reproduce with modification from [10].) D. Simulated cyclic voltammetry response at a nanoelectrode with and without an electrical double layer close an electrode surface in red, and far from an electrode surface in black. (Reproduced with modification from [16].)

210 nm nanogap shown in Figure 4A even though the Debye length at this ionic strength is only \approx 3 nm.

Typically, in high ionic strength solutions the electrical double layer in compressed and composed primarily of the ions of the supporting electrolyte. However lowering the supporting electrolyte concentration increases the size of the electrical double layer and also changes the double layer composition. The electrical double layer has two primary effects on redox cycling, it concentrates or dilutes (depending on the charge state of the redox species) the redox species in the nanogap and it alters the transport of the redox species across the nanogap by contributing to the migration of charged redox species (which can help or hinder redox cycling depending on the charge of the particular redox couple) [28]. We have recently reported both current enhancement and current depression when lowering of ionic strength in a lithographically fabricated nanogap electrochemical cell [8,29]. Currents were reduced with decreased ionic strength for the FcTMA^{+/2+} redox couple as shown in Figure 4A but increased for the hexaamineruthenium(III) ($\widetilde{Ru}(NH_3)_6^{2+/3+}$) redox couple as shown in Figure 4B. A very similar effect was observed by Bohn and coworkers with the $Ru(NH_3)_6^{2+/3+}$ redox couple, as is shown in Figure 4C [10,30]. Similar concentration effects have been recently reported by Lu and Zhang using a thin-layer cell geometry with a single electrode confined within a nanometric volume [31[•]].

In the FcTMA^{+/2+} redox cycling at low supporting electrolyte concentrations the oxidation of the positively charged FcTMA⁺ species occurs at an electrode held significantly positive of the potential of zero charge, while the reduction of the FcTMA²⁺ species occurs at an electrode held around the potential of zero charge. The electrode held very positive of the potential of zero charge decrease the concentration of redox species in the nanogap by excluding the positively charge ions from the nanogap. In addition the positively charged electrode induces migration which acts to hinder the diffusion of FcTMA⁺ to the positively charged electrode surface. Both the ion depletion in the nanogap and the migration of charged species in the nanogap contribute to a decrease in current with a decrease in ionic strength. However, in the ${\rm Ru(NH_3)_6}^{2+/3+}$ redox couple the reduction of the positively charge ion occurs at an electrode surface held significantly negative of the point of zero charge and so leads to the increase in the redox species concentration within the nanogap due to electrostatic ion enhancement as well as an increase in redox cycling due to the addition of a migration term in the mass transport between the two electrodes. The effect of the electrical double layer on redox cycling of the FcTMA^{+/2+} and Ru(NH₃)₆^{2+/3+} couples has been modeled using finite-element simulations, which quantitatively predict the observed current enhancements and depressions [8,29].

Recent work by Mirkin and coworkers also emphasized that the effect of the electrical double layer in a nanogap must be considered when calculating the electrontransfer rate constant, especially for highly charge redox species [16,32]. In a nanogap created using the scanning electrochemical microscopy approach, Mirkin showed that the shape of a cyclic voltammogram, such as those shown in Figure 4D, is strongly influenced by the electrical double layer. When calculating the electrontransfer rate the double layer must be considered (i.e., a Frumkin correction added) otherwise erroneous rate constants could be calculated.

Also of note is work by Amemiya and coworkers who recently reported an asymmetry in cyclic voltammograms for the FcTMA^{+/2+} redox couple in a nanogap between a Pt electrode and a highly orientated pyrolytic graphite (HOPG) substrate [33]. This promoted ongoing debate about importance of contamination of the HOPG surface vs adsorption of the redox species on the electrode and surrounding glass surfaces [33–35].

In summary, the recent work involving redox cycling in nanogap electrodes has highlighted the importance of ion enhancement effects generated by the electrical double layer as well as the effect of migration on the redox cycling. Nanogap electrochemical cells provide a precisely controlled platform to probe electrochemical reactions in confined spaces. In particular nanogap electrochemical cells can be used to understand the performance of energy conversion and storage technologies (such as super capacitors, batteries and fuel cells) where nanoporous and nanostructured electrodes which confine electrochemical reactions to nanometric spaces are often used to improve performance.

Conclusions

Based on the well-established idea of a twin-electrode thin-layer cell, nanogap electrochemical cells with widths of less than 100 nm provide a power tool for nanoelectrochemical measurements. In particular, as we have highlighted the electrochemical response of a single redox species as well as effect of the electrical double layer can be probed using a nanogap of less than 100 nm. Look-

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