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Review Article

Nano- and micro-gap electrochemical transducers: Novel benchtop fabrication techniques and electrical migration effects

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Redox feedback mechanisms can be exploited in electroanalytical detection right to the limit of single molecules being observed. The process relies on anode and cathode being placed extremely close together to minimize diffusion time. In addition to the more complex and expensive nanofabrication tools, there are attempts of “benchtop” micro-gap and nano-gap fabrication to exploit deposition and etch reactions in the assembly. An overview is given summarizing recent methodology development and emerging applications in electroanalysis. One important implication of a very close anode-to-cathode distance is migration of ions in a strong electric field when no electrolyte is used, leading to ion accumulation and a change in signal amplification. Phenomena of this type and geometry/functional implications are considered.

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Introduction

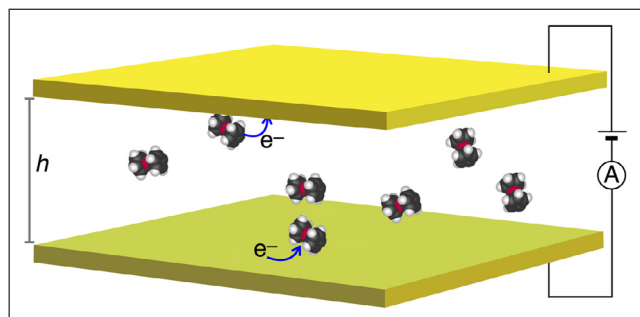
Confining electroanalytical detection to the small volume of a micro- or nano-channel cavity leads to many advantages compared to conventional macroscopic sensing methods: smallest sample volumes can be handled, and sensing elements can be integrated in microfluidic lab-on-a-chip analytical platforms. Importantly, miniaturized electrochemical transducers can be extremely

sensitive when *two* individually addressable electrodes are integrated (see [Figure 1](#)). By biasing these two electrodes at the respective oxidation and reduction potentials of a reversible electrochemically active analyte (or indeed at oxidation and reduction potentials that lead to redox cycling even for chemically irreversible reactions), this species can undergo repeated oxidation and reduction reactions. This method leads to a great amplification of the Faradaic current contributed by each analyte molecule. The current is limited by the time t of analyte diffusion in between the two electrodes $t = h^2/2D$ (D : diffusion coefficient). This time and the detected current scale (inversely) quadratically with the inter-electrode distance h ; thus, reducing the inter-electrode distance to the nano-scale may lead to a several thousand-fold increase in signal.

This amplification principle has been utilized in thin-layer cell electrochemistry more than fifty years ago [1]; more recently, the application of micro-structuring technology [2] for the fabrication of electrochemical transducers has led to the first nano-gap thin-layer cell in 2007 [3^{*}]. In addition to current amplification by redox cycling, micro- and nano-cavity dual-electrode devices share the characteristic of a *geometric confinement* of analyte molecules, i.e., they are “trapped” in between the electrodes at least for a short period of time as opposed to the case of “open” interdigitated [4] electrode configurations. The research in nano-gap electrochemical devices was originally motivated by increasing the sensitivity toward all-electrical detection of single molecules [5,6]; these devices also enabled stochastic mesoscopic sensing due to small numbers of confined molecules [7], and they have been used for biosensing [8,9] and orthogonal sensing in combination with optical microscopy [10]. All of these developments have all been reviewed recently [11–20].

The fabrication of electrochemical transducers with inter-electrode distances in the nano- and low micro-meter range typically requires complex lithographical fabrication techniques [2,21] in the cleanroom. However, recently several different fabrication techniques have emerged, enabling often a much more straightforward manufacturing approach. Also, typical redox cycling experiments were conducted under the condition of a high concentration of background electrolyte to avoid the complex influence of a Debye double layer at a length scale

Figure 1



Schematic of a dual-electrode configuration for efficient redox cycling of reversible electrochemically active molecules. Analytes (such as ferrocene) in solution are repeatedly oxidized and reduced as they diffuse in a space confined by two electrodes separated by a distance h of tens of nanometers up to several micrometers. The high rate of electron transfer reactions leads to a highly amplified Faradaic current of each analyte molecule.

similar to inter-electrode distances. Recently though, migration in an electrical field in combination with electron-transfer reactions was explored in electrolyte-free environment. In this opinion article, we review these two aspects of nano-/micro-scale electrochemical transducers: novel fabrication techniques, and electrical migration effects in miniaturized dual-electrode configurations.

Fabrication technologies for nano-/micro-scale dual-electrode transducers

Although nanofabrication tools are powerful and advanced (see lithography techniques employed in the CMOS chip industry) there are opportunities for low cost fabrication tools including 3D- and inkjet printing and electrodeposition. Microfabrication has been successfully applied for nano-channel devices [3•] and for large arrays of recessed dual-ring electrodes [22]. The latter approach has also successfully been coupled to single molecule photo-electrochemistry by inserting the transparent array into a spectrometer [10]. These are exceptional achievements and pioneering attempts to explore stochastic information obtained from single molecule events. However, for the detection of single molecule information the sample volume needs to be small and therefore the concentration of analyte relatively high. In order for redox cycling to be useful in amplification of ensemble electroanalytical signals a larger sample volume needs to be probed, which suggests the use of large arrays or dual-plate devices with a relatively large area.

Attempts to develop electrodeposition processes to grow dual-electrode sensors (by connection or disconnection

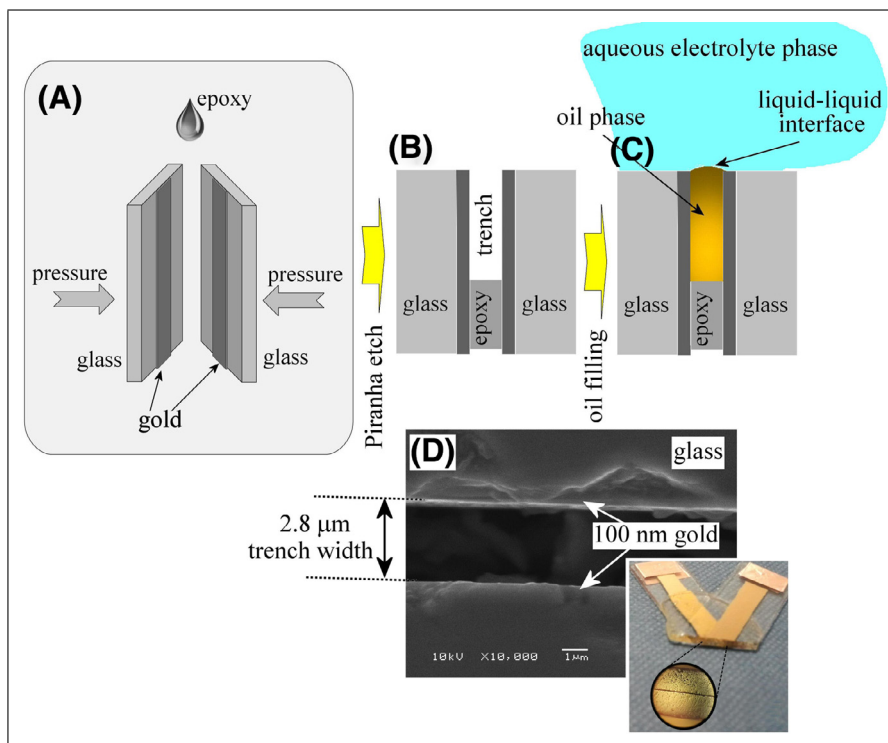
methods [23]) were hampered by the awkward electrode geometries generated under these conditions. Much improved current amplification effects were found when developing dual-plate electrode sensors [24••,25].

Figure 2 shows the fabrication principle with two gold plated glass slides being pressed together and sealed with an epoxy layer. After slicing off the end and back-etching with Piranha solution, a microtrench is exposed. The inter-electrode gap can be between 1 to 50 μm and the depth of the trench (etching time-dependent) has a significant effect on enhancing the amplified currents. Devices have been produced for gold–gold [27], platinum–platinum [28], and boron-doped diamond–boron-doped diamond configurations [29]. The depth of the microtrench has an interesting effect on the redox processes. Due to one side of the microtrench being open and exposed to the solution phase oxygen can diffuse in. But the oxygen levels deplete within the microtrench (due to consumption at the electrode surface) and within a depth about 3–5 times the inter-electrode spacing oxygen can be considered depleted and the conditions become anoxic [30]. Accordingly, the chemistry of redox cycling changes locally. In particular, for the case of voltammetric detection of HS^- it can be observed that depletion of oxygen changes the redox cycle chemistry and the current response.

New types of templates have emerged for example based on nano-sphere aggregates [31], and these can be employed also in controlling the gap between two flat electrode surfaces (dual-plate). Park *et al.* [24••] have shown that silica beads can be used as spacer components to separate two flat electrodes by a very well defined gap. Figure 3 shows the assembly principles and typical scanning electron micrographs.

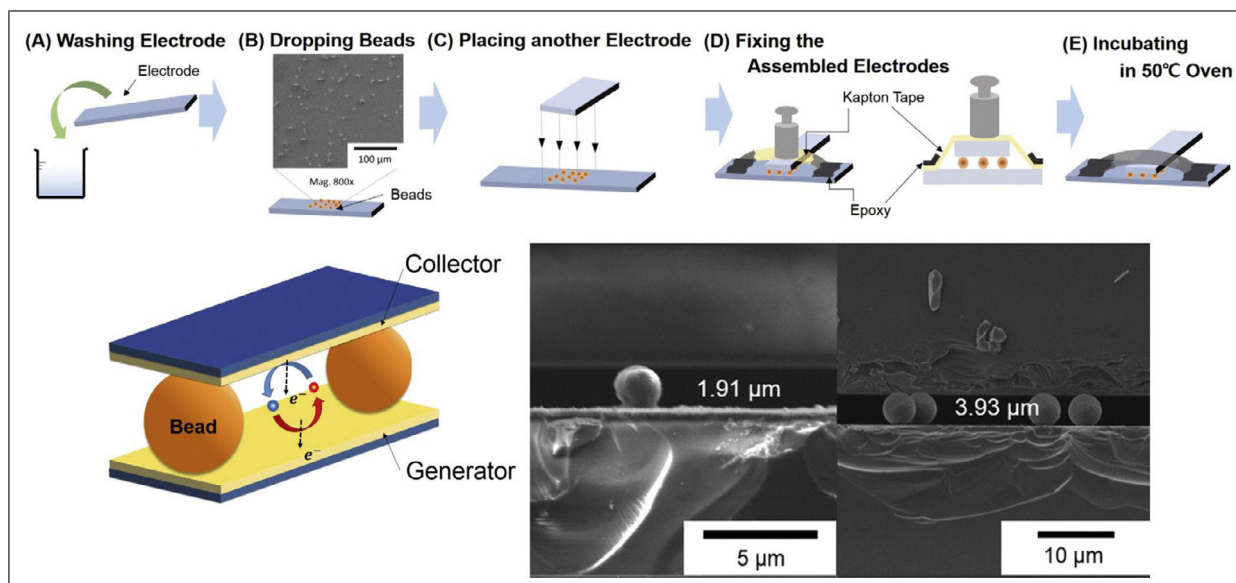
A very powerful emerging fabrication tool for electrochemical devices is 3D- and inkjet printing [18,32••,33]. In order to harness inkjet printing in the development of generator–collector electrode assemblies Adly *et al.* [32••] suggested a five-step strategy (Figure 4). Initially, the gold and carbon contacts are generated. Then a passive layer leaves gold exposed. A polystyrene (PS) beads layer defines the nano-gap, and a carbon electrode is printed on top. The assembly is open through a porous carbon electrode to the outside electrolyte solution. When scanning the potential of the carbon electrode and fixing the underlying gold electrode, well-defined generator–collector current responses are obtained, for example for a 0.5 mM ferrocenedimethanol solution (Figure 4D). A similar concept has recently also been developed based on platinum leaf electrodes with sufficient micron-sized porosity to allow electrolyte through a track-etch membrane spacer [34]. A sandwich Pt–membrane–Pt was sealed into polymer with one of the Pt leaf electrode open to the electrolyte solution.

Figure 2



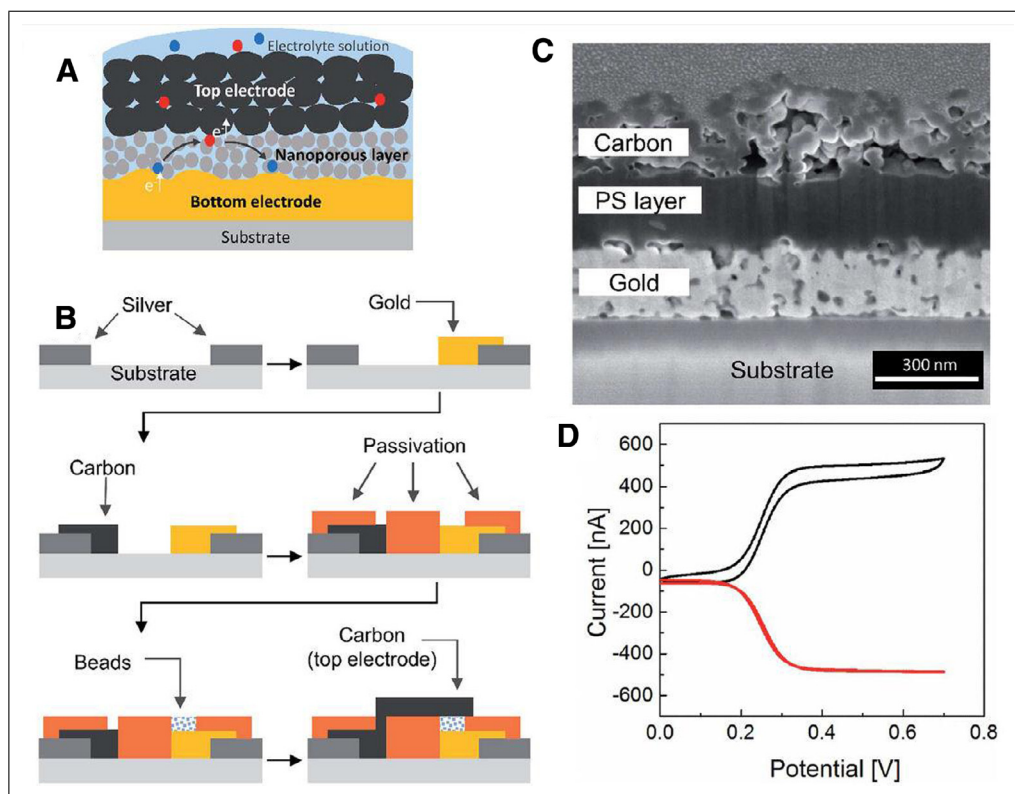
(A) Schematic drawing of a dual-electrode assembly resulting in two gold electrodes with epoxy separator. (B) Piranha etch solution allows a trench to be exposed for electrochemistry. (C) Oil filling the trench allows redox cycling experiments at the oil/water interface. (D) A typical scanning electron micrograph and photographic image of the gold-gold dual-plate microtrench electrode. Copyright 2013 Wiley. Used with permission from Ref. [26].

Figure 3



Schematic drawing of the assembly process (A-E) of bead-separated dual-plate electrode systems. Below: schematic drawing indicating the redox cycling process and scanning electron micrographs showing beads as separators. Reprinted from Ref. [24], Copyright (2016), with permission from Elsevier.

Figure 4



(A) Schematic drawing of an inkjet printed nano-gap electrode. (B) Assembly schematic. (C) Scanning electron micrograph of the nano-gap electrode in cross-sectional view. (D) Voltammetric response (scan rate) for aqueous 0.5 mM ferrocenedimethanol showing carbon electrode (black; scanning potential) and gold electrode (red; fixed potential) currents. Reproduced from Ref. [32••] – Published by the Royal Society of Chemistry.

Migration effects for nano-/micro-scale dual-electrode transducers at low electrolyte concentration

Most measurements and experiments employing micro-fabricated dual-electrode devices were conducted under the condition of a high concentration of background electrolyte. This condition was chosen to characterize the devices without the complex influx of an electric field and migration of ions, and – in the case of nano-channel devices – to prevent a feared mechanical collapse of the gap between the opposing electrodes due to electrostatic attraction. In such a geometry, a typical potential difference of 0.5 V across a 100 nm distance corresponds to a strong electric field of $E = 5 \text{ MV/m}$.

For several reasons migration at electrolyte-free conditions is an exciting topic to explore: 1) microfabricated inter-electrode distances approach the Debye length of the electrical double layer; therefore, nano-gap transducers can be an ideal system to study ion transport close to charged surfaces. 2) Electrical migration can lead to a more efficient transport toward the electrode surface, which increases the Faradaic current per molecule [35] and, thus, leads to an increase in sensitivity which

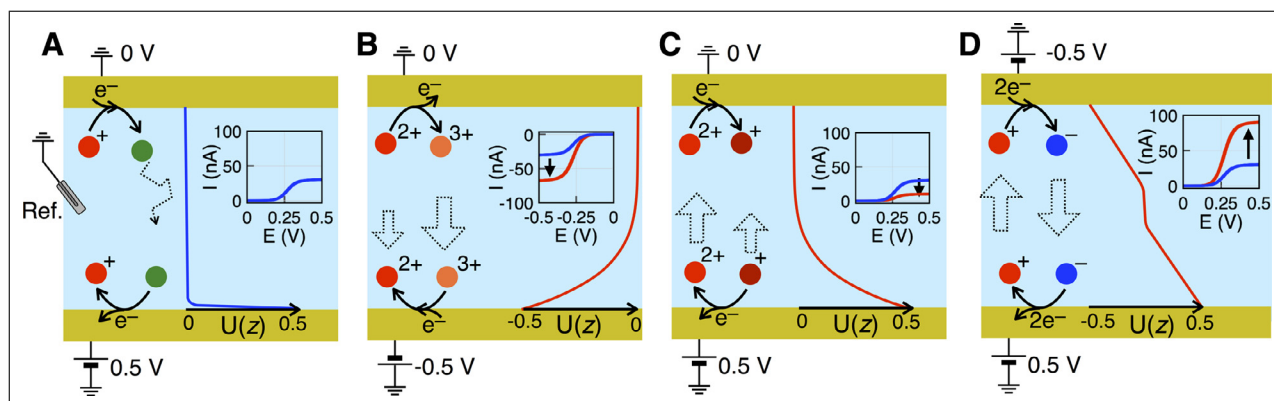
is highly beneficial in single-molecule electroanalysis. 3) Electrostatic effects can lead to an additional boost in current amplification by *accumulation* of ions [36].

Migration takes place within the Debye length λ_D of the electrical double layer, which, at low electrolyte concentrations, can extend considerably into the nano-channel. λ_D is given as [37]

$$\lambda_D = \sqrt{\frac{\epsilon_r \epsilon_0 k_B T}{e^2 N_A \sum C_i z_i^2}} \quad (1)$$

Here $\epsilon_r \epsilon_0$ is the electric permittivity, k_B the Boltzmann constant, T the temperature, e the elementary charge, N_A the Avogadro constant, C_i the concentration and z_i the charge number of ions i . Therefore, a 100 mM concentration of monovalent electrolyte reduces the Debye length to 1 nm at both electrode surfaces (negligibly small compared to a 100 nm inter-electrode distance), but λ_D increases to 30 nm for a 100 μM monovalent electrolyte or analyte concentration, spanning 60% of a 100 nm high nano-channel. An expected increase in the Faradaic limiting current can be directly estimated by comparing the

Figure 5



Prototypical schemes of reactions and migration of ions in nano-gap transducers. A) Left: reduction (top) and oxidation (bottom) of an electrochemically active molecule with $z=0, 1$ at a high electrolyte concentration. Right: electric potential U across the nano-channel. B) Electrolyte-less condition of $z=2, 3$ leading to a current *amplification* due to migration (dashed arrows) of $3+$ ions to the bottom electrode [42^{••},44]. C) Electrolyte-less condition of $z=1, 2$ leading to a *reduction* in Faradaic current as $1+$ ions are repelled and depleted at the bottom electrode [45^{••}]. D) Anticipated electrolyte-less condition of $z=\pm 1$ leading to a strong current *amplification* as transport of both ions is aided by migration. The insets sketch the change (blue $\rightarrow$ red) in cyclic voltammograms when removing the background electrolyte, recorded at a sweeping bottom electrode.

electrophoretic and diffusive travelling times of an analyte ion across the nano-gap. The mobility μ_e , approximated by [38] $\mu_e = \frac{qD}{k_B T}$, (q : molecular charge), leads to a migration velocity of a typical analyte ion such as oxidized ferrocenedimethanol of $\mu_e \cdot E \approx 10$ cm/s, i.e., a *migration* time of 1 μ s across a 100 nm distance. This value compares favorably to a longer *diffusion* time of $(100 \text{ nm})^2/2D \approx 10$ μ s.

The diffusional-migrational transport in an electrolyte-less thin-layer cell was first modeled by Hyk and Stojek [39] and others [40,41]. In a first experimental study by the Bohn group, Ma *et al.* [42^{••}] demonstrated an increase in redox cycling current of 50% for a $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ analyte due to increased migration in a recessed ring-disk electrode geometry ($h=150$ nm). $\text{Ru}(\text{NH}_3)_6^{3+}$ transport to electrodes is enhanced, while the transport of $\text{Ru}(\text{NH}_3)_6^{2+}$ is impeded, but to a smaller degree (see Figure 5B, Figure 5 compares different migrational effects). It was observed that the enhancement of the limiting current increases with lower analyte concentrations as the double layer starts to extend significantly. Moreover, an additional effect was observed: ions *accumulate* in the nano-channel, i.e., positive ($z=+3$) analyte ions move into the nano-channel to counterbalance negatively charged electrode surfaces in order to maintain electroneutrality [43]. Both effects together lead to a high enhancement factor of approximately 100 when comparing the limiting current of redox cycling obtained in absence and presence of supporting electrolyte.

Xiong *et al.* showed that cyclic voltammograms under electrolyte-less conditions in nano-gap devices exhibit

a more complex shape [45^{••}]: the limiting current of $\text{FcTMA}^{+/2+}$ (in acetonitrile) *decreases* at lower electrolyte concentrations as FcTMA^+ is repelled from the anode and depleted (see Figure 5c). Increasing the oxidation potential beyond the onset of the diffusion-limited plateau to higher overpotentials leads to a *decrease* in current as migration repels FcTMA^+ stronger. A reduction of the limiting current by migration was also suspected for redox cycling in a nonpolar medium, in which very low electrolyte dissociation can lead to a large Debye length even at a high salt concentration [46].

In nano-pore electrode arrays, ring electrodes can lead to ion permselectivity as all analytes passing into the pore have to react at this ring electrode before passing on into the pore which is closed by a bottom electrode [47]. In combination with a small pore size, this effect can lead to an enormous accumulation and current amplification. Such accumulation has also been used for selective sensing [48] and also occurs in nano-cavities with only a single electrode.

In addition to studies at lithographically fabricated electrodes, experimental work at benchtop-fabricated electrode systems has been reported under conditions of no/low intentionally added electrolyte. Recent data has been reported for dual-plate micro-gap electrodes indicating that electrolyte effects remain small compared to other types of effects [49]. In fact, the dual-plate electrode configuration may be useful for electroanalysis under conditions where supporting electrolyte levels fluctuate. Another intriguing application has been suggested for a dual-plate Au/Pt electrode system separated by 37 nm

with porous silicon nitride filling. Due to the close proximity of the electrodes effective water splitting (into H₂ and O₂) was possible in pure distilled water [50*].

Conclusion and outlook

Benchtop fabrication of electroanalytical sensor devices with redox feedback amplification is possible down to sub-micron dimensions and it offers a novel strategy to suppress interference signals while amplifying signals due to low concentration and/or for short-lived species. Although some examples of redox amplification sensing are now reported, there is likely to be a much wider range of potential applications. Aspects of chemical reactivity in nano-gaps will be very interesting to explore in more detail. Chemical reactions that occur under high electric field conditions are known for example at bipolar polymer interfaces [51] and in bipolar electrochemistry in general [52], and a wider variety of similar field-driven reactions may be possible also under dual-plate nano-gap electrochemical conditions. Furthermore, the time scale for reactions coupled to diffusion from anode to cathode can be extremely fast to allow new types of electro-organic or synthetic dual-plate processes without adding supporting electrolyte. In all of these cases electric field and migration phenomena are important when high field gradients are combined with resistive media and high currents. Electric field and migration effects can be detrimental to the overall device performance. In nano-gap and micro-gap devices, however, field and migration effects may also be advantageous (diffusion-migration currents can be increased; double layer effects allow analyte accumulation, conditions of high electric field can act catalytically, etc.). When performing experimental work with nano- and micro-gap devices it is advisable to always perform sets of experiments with a different concentration and/or different type of electrolyte to avoid/identify these effects.

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- Paper of outstanding interest.

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