Redox-Driven Reversible Gating of Solid-State Nanochannels

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S *Supporting Information*
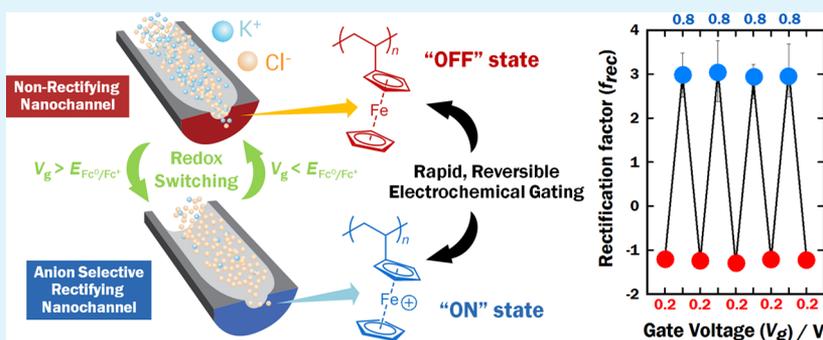
ABSTRACT: The design of an electrochemically addressable nanofluidic diode is proposed, which allows tunable and nanofluidic operations via redox gating under electrochemical control. The fabrication process involves the modification of an asymmetric gold-coated solid-state nanopore with a thin layer of a redox polymer, poly(vinylferrocene) (PVFc). The composite nanochannel acts as a gate electrode by changing the electrochemical state and, consequently, the conversion/switching of ferrocene into ferricenium units upon the application of different voltages. It is shown that the electrochemical input accurately controls the surface charge density of the nanochannel walls with a predictable concomitant effect on the rectification properties. PVFc-based nanofluidic devices are able to discriminate the passage of anionic species through the nanochannel in a qualitative and quantitative manner by simply switching the redox potential of the PVFc layer. Experimental data confirmed that a rapid and reversible modulation of the ionic transport regimes can be easily attained by changing the applied potential. This applied potential plays the role of the gate voltage (V_g) in field-effect transistors (FET), so these nanofluidic channels behave as ionic FETs. Depending on the V_g values, the iontronic behavior can be switched between ohmic and diode-like regimes. We believe that this system illustrates the potential of redox-active polymers integrated into nanofluidic devices as plausible, simple, and versatile platforms to create electrochemically addressable nanofluidic devices for multiple applications.

KEYWORDS: nanofluidics, electrochemical actuation, ionic diodes, ionic rectification, nanofluidic devices, solid-state nanopores, nanochannels, redox polymers, poly(vinylferrocene)

INTRODUCTION

During the past years, there has been an increasing interest in developing nanofluidic devices capable of controlling the transport of ionic species by experimentally controllable inputs or stimuli, such as pH, temperature, light, or the presence of certain molecules in solution.[1,2] A part of the interest in this area of research stems from the fact that solid-state nanochannels (SSNs) represent key novel nanoarchitectures in different applications such as biosensing,[3] water transportation,[4] or energy conversion.[5] Inspired by biological ion channels, their biological counterparts, many research groups have studied strategies for gaining control over the ionic transport through the SSNs, exploring the frontiers of the so-called biomimetic nanofluidic systems.[3,6−16] In this context, many efforts propelled the rational development of synthetic

nanochannels mimicking some properties of the biological protein channels, such as rectification of the ionic current, gating effects, and modulation of the ion transport by specific targets or analytes.[17] As an example, the disruption of the geometric and charge symmetry renders asymmetric electric potential profiles along the nanochannel axis, which promotes variable conductance depending on the polarity of the applied transmembrane voltage.[18−20] In that case, the transport of a particular type of ion (cation or anion) is selectively favored yielding cation-driven or anion-driven currents (iontronic diode-like behavior).[21] Recently, it has been also shown that

asymmetric current−voltage responses can be also obtained not by producing asymmetric nanochannels but by introducing asymmetry at the reservoir geometry level.[22] There are also several methods for inducing current modulation or gating effects on the ionic current by the appropriate integration of molecular systems to the walls of the channels,[23−26] leading to great versatility of responses.[27] Thus, from different chemical strategies, nanopore systems with responsiveness to a variety of stimuli such as pH changes, light, temperature, or the presence of a particular analyte have been developed.[21,28−34]

Within this framework, particularly interesting is the development of nanofluidic channels able to precisely modify their ionic transport by selecting the values of controllable external variables. Among all the stimuli methodologies, the electrochemical stimuli-based strategy is particularly promising because the redox potential can be easily tuned by changing the applied electric potential. Concomitantly, the use of redox-active bistable molecules that can be externally switched between two states with different properties can lead to active elements that can be controlled by electrochemical means. By way of example, the use of electroactive molecules has been previously explored in molecular electronics by their incorporation in three terminal junctions followed by the application of a voltage to a gate terminal, thus resulting in the modulation of the molecular charge and the current passing through two contacts.[35,36]

This notion has been vastly explored in molecular electronics, but the extrapolation of this concept to nanofluidic devices has been scarcely explored. Exciting opportunities are revealed when we think in this manner. Electrochemistry offers alternative means to control the chemical features of nanofluidic channels and provides a complementary perspective from which new facets of the emerging field of "field-effect nanofluidics" can be seen.[37−39] If we consider that, depending on the molecule, redox events behave in a predictable manner[40] because their oxidized and/or reduced states are reasonably stable then by changing the applied potential, we would be able to easily modulate the surface charge on the nanochannel walls and operate the nanofluidic readout with a fast response and high efficiency. Furthermore, as the applied potential plays the role of the gating voltage (V_g) in field-effect transistors, these nanofluidic channels would operate as field-effect nanofluidic diodes or ionic FETs[41−43] and contribute much interest.

There are some interesting examples in which the gate voltage was employed to modulate the transmembrane current. These examples were based on the deposition of metals or semiconducting materials into the nanochannels.[43−46] However, such systems require rather complex fabrication technologies. On the other hand, the integration of a redox polymer layer appears as a simple and straightforward strategy for introducing active elements for transducing the gate voltage into transmembrane current changes, even for small V_g variations.

Electroactive polymers refer to a family of materials that can be reversibly oxidized and reduced.[47] These materials are frequently classified into conducting polymers (CPs) and redox polymers (RPs).[48] On one side, CPs have an extended double-bond conjugation, and they present metallic-like conductivity when doped to a certain degree (oxidized or reduced). They are commonly synthesized by chemical or electrochemical oxidation of an aromatic monomer, and typical examples of this kind of polymers are polyaniline (PANI),

polypyrrole (PPy), and poly(3,4-ethylenedioxythiophene) (PEDOT). On the other side, RPs are not conducting materials, but they present redox centers chemically bound to the polymer matrix. These centers can be part of the polymer structure, as in poly-o-aminophenol (POAP),[49] or metallic complexes bound to the polymer chain, as in the case of the osmium complex-modified polyallylamine (OsPA),[50] and the ferrocene moieties in poly(vinyl ferrocene).

Although there are some recent examples approaching the combination of conducting polymers and nanoarchitectures, particularly for sensing applications,[51,52] the integration of such CPs into nanofluidic devices has been scarcely explored with just few recent examples. In this sense, Pérez-Mitta et al. developed a voltage-responsive nanochannel by modification of a nanochannel with PANI.[53] In that work, a PANI film was electrosynthesized on a Au-sputtered polycarbonate single pore membrane. The highly rectifying behavior obtained was ascribed to the decrease of the effective pore diameter and the presence of positive charges on protonated PANI. By tuning the applied potential to the metallized membrane, the redox states of PANI could be easily changed. In that way, a continuous increment of the rectification ratio based on the PANI oxidation degree was achieved. Furthermore, a reversible gating of the transmembrane current was obtained by switching the applied potential between values corresponding to the completely reduced (poorly protonated) and completely oxidized (highly protonated) states.

Another redox potential-responsive system was prepared on Pt-sputtered AAO nanochannels by electropolymerization of a polypyrrole (PPy) coating.[54] By oxidizing the coating, the initially neutral PPy turns to a polycationic form due to the formation of polarons and bipolarons in its structure. Thus, a reversible switching of the rectification efficiency and the transmembrane ionic current was obtained by changing the PPy oxidation state. More recently, an electrically actuated hydrophobically induced gating mechanism in AAO nanoporous membranes was achieved by electropolymerization of PPy in the presence of perfluorooctanesulfonate anions (PFOS⁻).[55] After ex situ oxidation in acetonitrile, the doping anions turn the PPy highly hydrophobic, whereas it is hydrophilic in the reduced state. As the ionic transport is sensitive to the wetting of the walls of the nanochannels, the transmembrane current measured in aqueous solution depends on the hydrophobic/hydrophilic state of the PPy films.

More recently, a completely new concept for gating effects in nanofluidic channels was presented.[41] In this case, the electrochemical modulation of the nanochannel transmembrane current was achieved employing an all-polymer device by chemical polymerization of PEDOT upon a conical etched PET nanochannel. The PEDOT layer does not only enhance the rectification properties of the nanopore but it also allows changing the surface charge state by using a bipotentiostat configuration. This means that for a given transmembrane voltage, the application of different gate potentials produces changes in the nanochannel ionic conductance, resembling a typical FET measurement. Owing to the rapid reversion and modulation of the surface charge by the gate potential, a simple and effective modulation of the rectification efficiency was achieved.

On the other hand, the integration of a redox polymer such as poly(vinylferrocene) into SSNs results particularly appealing due to the fact that this electroactive polymer bearing organometallic redox centers displays a remarkably fast and
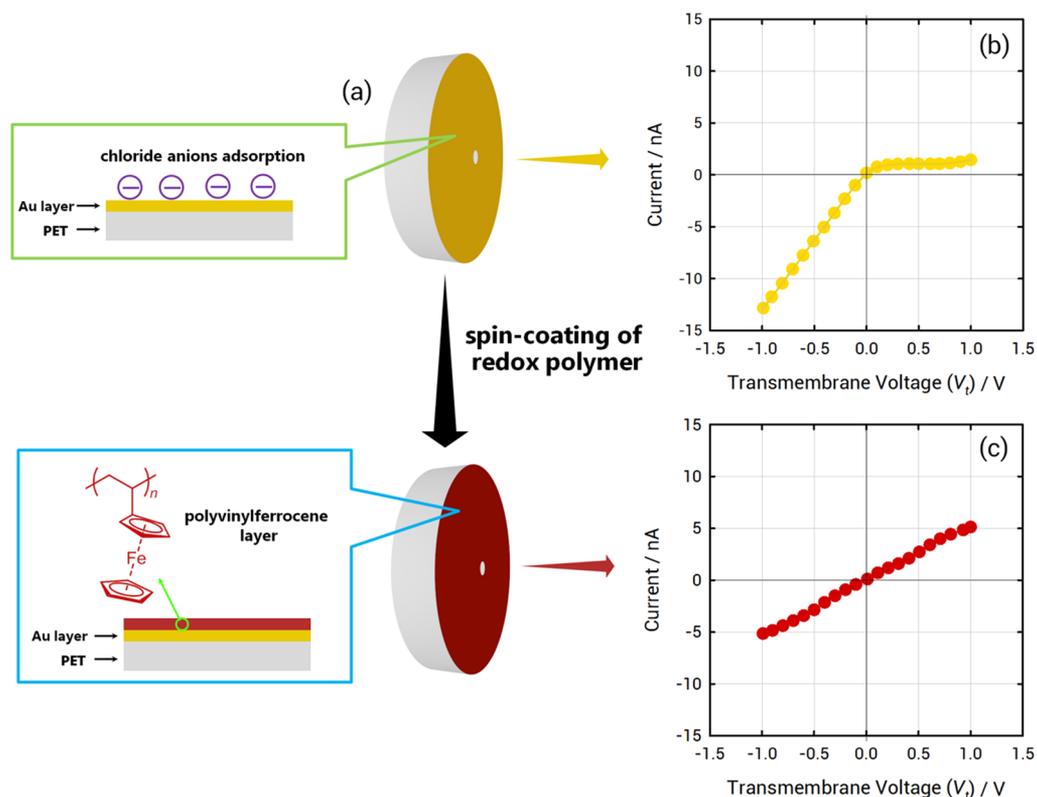
Figure 1. (a) Schematic representation of the metallization and PVFc-modification of the PET membrane. $I–V$ characteristics of the nanochannel (in 0.1 M KCl) (b) before and (c) after modification with a PVFc layer.

reversible bistable response as ferrocene exhibits two accessible redox states (i.e., neutral reduced state and positively charged oxidized redox state). As such, the intrinsic characteristics of ferrocene units[56] render them unique candidates for creating redox-switchable nanofluidic devices.

Herein, we present the development of a redox polymer-based FET-like nanofluidic system obtained by incorporating PVFc onto the Au-sputtered surface of asymmetric PET nanochannels. As mentioned above, PVFc is a redox polymer in which the electroactive moiety (ferrocene unit, Fc) is covalently bound to the polymer backbone.[57−60] This redox unit can be reversibly switched between the neutral ferrocene and the cationic ferricenium states by externally changing the applied potential. Thus, the inclusion of this redox polymer allows obtaining a rectifying channel whose transport can be easily modulated by an external input: the applied potential, which behaves as the gate voltage in FETs. The goal of this work is not only to demonstrate that the bistable characteristics of ferrocene units enable a well-defined, electrochemically controlled "ON/OFF" response of the nanofluidic device but also to show that the applied potential offers an interesting means to control the equilibrium between ferrocene and ferricenium species and consequently accurately tune the output ionic signal of the nanofluidic diode. To the best of our knowledge, this is the first example describing the integration of a redox polymer into a nanofluidic device as a strategy to fabricate nanofluidic diodes with rapid, reversible, and tunable gating characteristics.

■ EXPERIMENTAL SECTION

Chemicals. Poly(vinylferrocene) ($M_w \approx 50$ kDa) was purchased from Polysciences Inc. KCl and NaOH were from Anedra, whereas

toluene was from Dorwil. All chemicals were of analytical grade and were used as received. All experiments were performed with Milli-Q water (18.2 MΩ cm).

Preparation of the Nanochannel. Bullet-shaped single pore nanochannels were prepared on PET membranes by ion-track etching.[61] First, 12 μm-thick PET membranes were irradiated by accelerated Au ions (11.4 MeV/nucleon) in the linear accelerator UNILAC, GSI, Darmstadt, Germany. Then, a surfactant-assisted asymmetric etching was performed for yielding bullet-shaped nanochannels.[62] In this procedure, the base side was soaked in 6 M NaOH, whereas the tip side was soaked in the same solution with the addition of 0.05% Dowfax 2a1 for 7−8 min at 60 °C. Finally, the membrane was thoroughly washed with pure water. The tip side of the membrane was then modified with a gold thin layer (ca. 80 nm) by sputtering.[53]

PVFc Modification. The metallized membrane was modified with PVFc by spin-coating on the metallized tip side. For this modification step, 100 μL of PVFc dissolved in toluene (1.6 mg/mL) was casted on the metallized face of the membrane, and a spin routine of 60 s at 1000 rpm with an initial acceleration of 250 rpm/s was applied. This process was repeated twice. Thereafter, the membrane was thoroughly washed with distilled water.

Experimental Setup and Measurement. In order to simultaneously control both the applied potential or gate voltage (V_g) and the transmembrane voltage (V_t), a bipotentiostat arrangement was employed.[41] Please refer to the Supporting Information for instrumental details on the $I–V$ curve acquisition in potential-control experiments.

Rectification Factors. The rectification efficiency was accounted by the rectification factor (f_{rec}), defined as indicated in eq 1.[63] This factor means the ratio between the transmembrane currents measured at transmembrane voltages of +1 and −1 V where the numerator corresponds to the high-conductance branch so that $|f_{rec}| \geq 1$, and it is multiplied by −1 if the high-conductance branch occurs at negative transmembrane voltages. In this way, the rectification factor is directly related to the surface charge density.[21]

$$f_{rec} = \pm \frac{|i(+1 \text{ V or} -1 \text{ V})|}{|i(-1 \text{ V or} +1 \text{ V})|} \qquad (1)$$

RESULTS AND DISCUSSION

After the gold sputtering on the tip side of the membrane, the bullet-shaped single nanochannel showed a nonohmic, asymmetric behavior (Figure 1). This effect has been already described in the literature and has been ascribed to the adsorption of chloride ions on the gold layer.[64,65]

The metallized side of the membrane (tip side) was then modified with PVFc by spin coating. X-ray photoelectron spectroscopy confirmed the modification of the membrane with PVFc (Figure 2). The XPS spectrum in the Fe 2p core
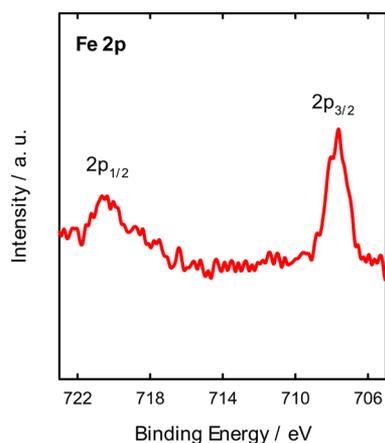
Figure 2. High-resolution XPS spectrum of the Fe 2p region of the PVFc-modified membrane.

region presents two peaks corresponding to the Fe $2p_{1/2}$ and Fe $2p_{3/2}$ components at about 720 and 708 eV, respectively, which are consistent with the presence of ferrocene moieties.[66,67] Moreover, ellipsometric measurements revealed that the thickness of the spin-coated film was 2.5 nm (see the Supporting Information).

As indicated in Figure 1, the coating with PVFc yields a change of the transmembrane currents, reducing the values of the high-conductance branch and, correspondingly, decreasing the rectification factor. As the hydrophobicity of the membrane remained practically the same after polymer coating (see the Supporting Information), the decrease of the transmembrane current can be assigned to the putative decrease of the tip diameter. On the other hand, the ohmic (linear) characteristics of the $I-V$ response can be attributed to neutral characteristics of ferrocene units. Even though this protocol is highly reproducible, in some freshly modified membranes, instead of a linear ohmic behavior, a low rectifying response has been observed. This could be assigned to some remaining adsorption of chloride anions.[68] Similar results have been reported for the case of carbon nanotube membranes coated with PVFc in which some remaining negative charges are observed after polymer modification, as revealed by zeta-potential measurements.[51]

PVFc presents two redox states depending on the applied potential or the presence of oxidizing or reducing agents in solution (Scheme 1). In the reduced state, the ferrocene moieties remain electrically neutral (Fc). However, when some oxidizing species are present or the polymer is subjected to positive (oxidizing) potentials, the iron center is oxidized, and

Scheme 1. Electrochemical Setup Used for the Experiments[a]
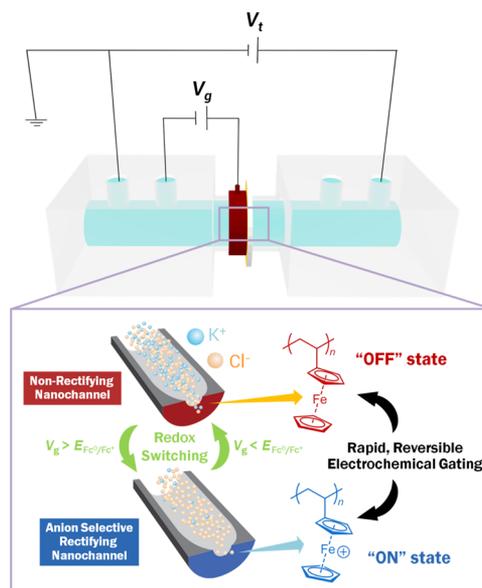
[a]Two hollow cells are connected through a single nanochannel-containing membrane. One of the compartments has an attached solution-isolated copper ring that electrically connects the PVFc layer acting as a gate and allows applying different gate voltages, V_g. V_t denotes the transmembrane voltage between the two cell compartments. The enlarged scheme describes the electrochemical conversion between ferrocene ("OFF", nonrectifying state) and ferricenium units ("ON", anion-rectifying state) when applying a gate voltage that ultimately produces a rapid, reversible switching of the ionic transport regimes.

the entire moiety turns to the ferricenium form with a net positive charge (Fc$^+$). In the case of polymer coatings, the oxidation process also yields the migration of counterions for keeping the electroneutrality within the films.[59,69,70] In principle, the charge compensation upon oxidation could happen by anion uptaking or cation expulsion. In the particular case of PVFc, it has been demonstrated that also the nature of the electrolyte influences the redox behavior in organic and aqueous solutions.[71−73] Although some studies indicate that some cation exchange also takes place during the redox switching of PVFc,[74] it is accepted that, for the ionic strength employed in this work (0.1 M KCl), the charge compensation is almost exclusively performed by anion exchange, that is, a permselective mechanism operates.[71] This anion entrance also results in swelling of the film upon oxidation.

The redox behavior of the PVFc films was studied by cyclic voltammetry (see the Supporting Information for details). The steady-state voltammogram of the PVFc-coated membrane in the conductance cell at 50 mV s^{-1} is presented in Figure 3a. There are some differences with respect to the voltammograms of PVFc films deposited on massive Au electrodes that are attributed to the higher electrical resistance of the Au layer sputtered on the polymer membrane. However, the redox behavior is the same as that obtained on massive Au electrodes, characterized by the presence of two voltammetric waves corresponding to the oxidation of ferrocene and reduction of ferricenium (see the Supporting Information). The dependence of the voltammetric peak current on the potential sweep rate is consistent with the presence of a surface-confined redox
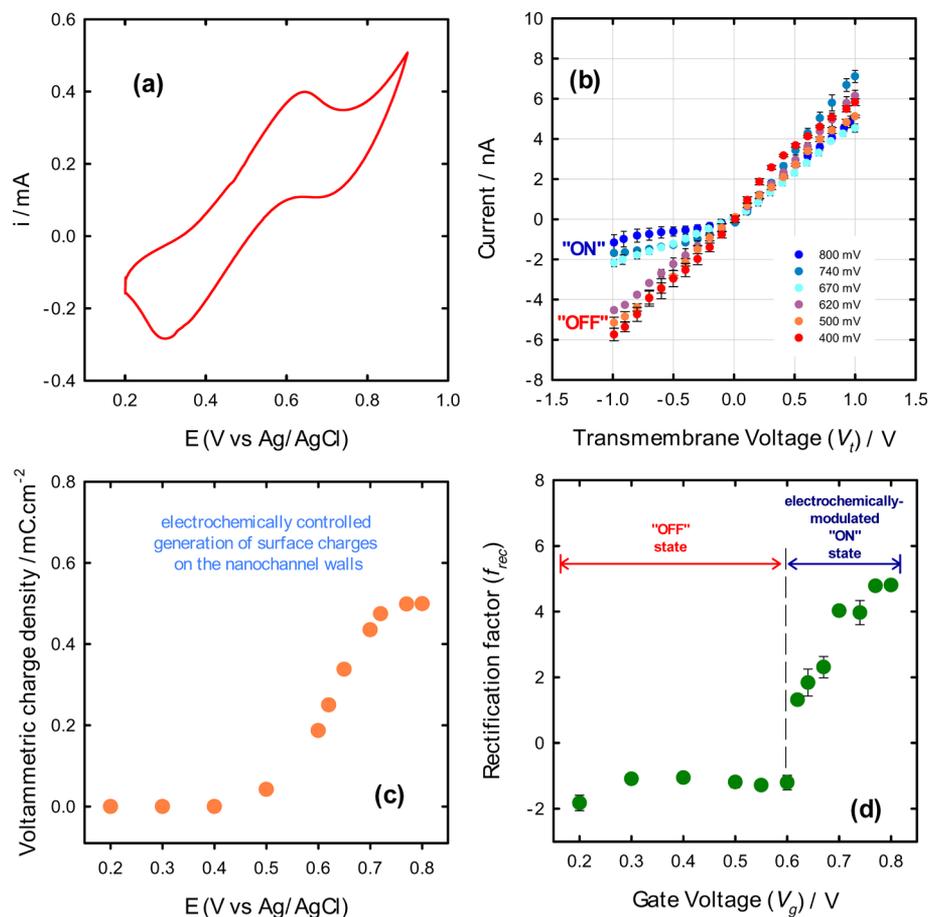
Figure 3. (a) Cyclic voltammogram of the PVFc-modified membrane recorded in the conductance cell at 50 mV s^{-1} in 0.1 M KCl. (b) $I-V$ response recorded at different gate voltages applied to the PVFc-modified nanofluidic channel. (c) Voltammetric charge density as a function of the applied potential associated to the Fc → Fc$^+$ + e$^-$ electrochemical process taking place on the membrane surface. (d) Rectification factor of the PVFc-modified nanochannel as a function of the gate voltage, i.e., applied potential.

couple,[75] which indicates that the film is extensively oxidized and reduced during the redox switching (Figure S3).

As illustrated in Scheme 1, our working hypothesis is that the redox state of the ferrocene units can be controlled by the applied potential, and this state can be switched from the "OFF" ohmic, nonrectifying state to the "ON" anion-rectifying state upon the interconversion of ferrocene units into ferricenium ones. The electrochemical generation of net positive surface charges on the nanochannels would, in principle, trigger the rectified transport of chloride through the nanofluidic device. The evaluation of the transport properties of the nanochannel at different applied potentials proved our hypothesis regarding the electrochemical switching of the transport regimes in the nanofluidic channels (Figure 3b). The transmembrane conductance of the PVFc-modified nanochannel was studied at different values of the applied potential to the membrane (different gate voltages) using a bipotentiostat setup (Scheme 1). Two regimes for the transmembrane iontronic behavior can be easily distinguished according to the gate voltage values. It can be observed that, for gate voltages more cathodic (negative) than the redox potential of ferrocene units, the organometallic centers remain reduced and the channel is neutral, thus conferring non-rectifying characteristics to the nanofluidic device. Then, upon increasing the applied potential beyond the redox potential of ferrocene units, the rapid formation of ferricenium moieties on

the nanochannel walls switches the transport characteristics into an anion-rectifying regime.

More specifically, for gate voltages lower than 0.6 V versus Ag/AgCl, the nanofluidic channel exhibits an ohmic behavior ("OFF" state). This is consistent with electroneutrality of reduced PVFc. On the other hand, for gate voltages higher than 0.6 V, a nonlinear behavior is observed with a rectification profile indicating a positive surface charge density. This is consistent with the appearance of positive charges due to the redox interconversion of ferrocene units into ferricenium ones at applied potentials higher than the redox potential for this redox couple. Thus, anion selectivity of the transmembrane current is obtained as a consequence of the presence of fixed positive charges in the tip region of the nanochannel, yielding cation depletion ("ON" state). It is important to clarify here that the ON/OFF transition does not refer to a high/low conductance switching but to a rectifying/nonrectifying (ohmic) regime alternation, which can be also described as anion-selective/nonselective transport switching.

It is interesting to note that the gate voltage not only controls the "ON/OFF" switching of the nanofluidic device but also controls the equilibrium between ferrocene and ferricenium species. In other words, by finely tuning the gate voltage or fine-tuning of the gate voltage (or applied potential), we should be able to regulate the surface charges on the nanochannel walls and consequently modulate the rectified
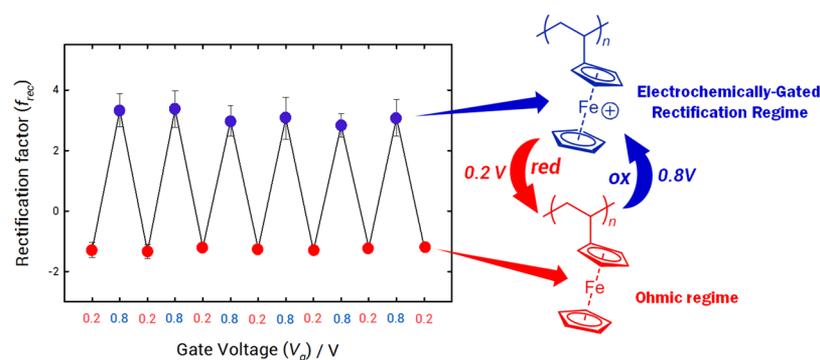
Figure 4. Reversibility of the potential-induced gating. The rectification factor of PVFc-modified nanochannels is switched by successive changes in the applied potential between 0.2 V (reduced state of the PVFc, red solid circles) and 0.8 V (oxidized state of the PVFc, blue solid circles). Switching between these two rectification behaviors implies that the nanochannel switches between an electrochemically gated rectification regime and an ohmic regime.
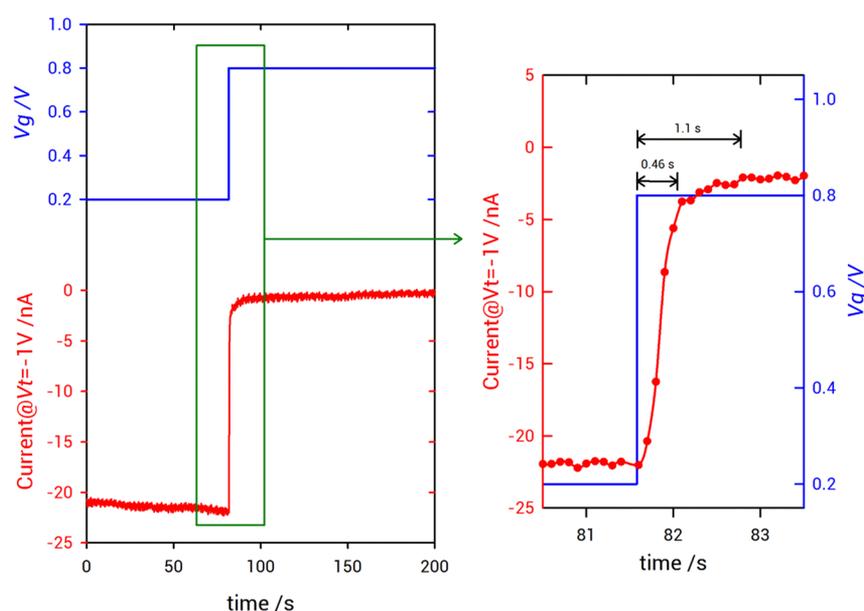
Figure 5. Time response of the transmembrane ionic current through the PVFc-modified nanochannel after changing the applied potential. The experiment was performed by simultaneously recording the applied potential (gate voltage, V_g) (perturbation) (upper panel, blue trace) and the transmembrane ionic current at a constant transmembrane voltage ($V_t = -1$ V) (response) (lower panel, red trace).

ionic signal. The electrochemical generation of ferricenium species on the nanochannel walls can be easily estimated from the Coulombic charge associated to the Fc → Fc$^+$ + e$^-$ process taking place at different applied potentials.

The increase in Coulombic charge associated to the conversion of Fc into Fc$^+$ units is directly proportional to the generation of cationic charges on the nanochannel walls. As already known, variations in the surface charge density have a strong impact on the rectification characteristics of asymmetric nanochannels. A direct comparison of Figure 3c,d reveals the strong correlation between the electrochemically generated surface charges on the nanochannel walls and the rectification properties of the nanofluidic device. It can be observed that the fine-tuning of the applied potential (or gate voltage) provides access to an "electrochemically modulated ON state" in which there is almost a linear correlation between the rectification factor and the gate voltage. As the gate voltage is increased, an increase in the population of the charged redox centers at the expense of neutral redox units is promoted, thus producing higher rectification efficiencies. Above ca. 0.75 V, the redox

polymer is completely oxidized, and a maximum charge density is attained (full conversion of redox units) with no further changes for higher potentials.

Results in Figure 3d show that simple regulation of the iontronic behavior of the transmembrane current can be produced by changing the electric potential applied to the membrane. By analogy with the effect of the gate electrode on FETs, the potential applied to the membrane can be thought as a gate voltage when considering its influence on the ionic transmembrane current.[41] Thus, the integration of a redox polymer to the nanofluidic device allows inducing a diode-like behavior just by simply changing the applied potential.

To explore the switchability of the nanofluidic system, the reversibility between the ohmic and rectifying regimes was studied by successively setting the applied potential at values corresponding to the reduced state (Fc, 0.2 V) and the oxidized state (Fc$^+$, 0.8 V) and by measuring the I−V response at each condition. Figure 4 shows the reversibility performance in terms of the rectification factors. As illustrated in this figure, the diode-like behavior can be selectively switched ON and

OFF by alternating the gate voltage in a reversible manner. These switching characteristics are highly reproducible; however, slight variations in the tip diameter and/or PVF thickness can cause sample-to-sample variations in transmembrane current values (see Figure S6). This sample-to-sample variability is often encountered in the nanofluidics literature, especially in the case of systems based on ion track-etched nanochannels. Despite this fact, we must point out that the electrochemically controlled "ON/OFF" switching is fully reproducible and was observed in all samples, as statistically assessed in different nanochannels (see Figure S7). The stability of the nanofluidic system allows measuring during several hours, but in some cases, extensive cycling can lead to gradual delamination of the conducting gold coating layer. In a similar vein, we have observed a slight decrease in the voltammetric integrated charge (which is proportional to the amount of electroactive material) after prolonged oxidation/reduction cycles. This observation has been interpreted in terms of the reversibility of the Fc/Fc^+ redox couple that is limited in aqueous electrolytes due to the side reaction of Fc^+ hydrolysis. This is the reason for the slight decrease in the rectification factors corresponding to the anion-driven diode-like states caused by a lower amount of Fc^+ moieties in the polymer as the number of switching cycles increases.

The switching dynamics of the gating effect was further studied by simultaneously recording the changes in the ionic transmembrane current for a given V_t caused by a rapid change in the gate voltage between extreme values (Figure 5). The transient results reveal that the ionic response of the nanofluidic device is almost instantaneous upon switching the applied potential, which reinforces the advantages of this electrochemically mediated gating mechanism for modulating the iontronic behavior in SSNs facing the design of smart nanodevices. Experimental data show that a stable ionic current is detected 1.1 s after switching the gate voltage, and 95% of that signal is detected within 0.46 s.

CONCLUSIONS

We have presented the development of a field-effect-like nanofluidic device based on the integration of a redox polymer onto the surface of a solid-state nanochannel. By modifying the Au-sputtered tip side of single-pore PET membranes with poly(vinyl ferrocene), a reversible modulation of the iontronic behavior by the applied potential has been demonstrated. By changing the potential applied to the PVFc-coated membrane, a precise control of the redox state of the ferrocene units can be achieved. The oxidation degree, in turn, modulates the surface charge density as the ferricenium moieties have a net positive charge. Thus, the regulation of the surface charge density is achieved by simply changing the applied potential. Furthermore, the presence of positive charges in the polymer film causes an asymmetric diode-like transmembrane response with anion selectivity. The applied potential influences the transmembrane ionic current in a manner similar to that of the gate voltage in field-effect transistors. In our case, by applying small gate voltages (<1 V), the rapid and reversible transition between ohmic and rectifying regimes is achieved.

The integration of redox polymers into solid-state nanochannels allows developing a new generation of devices with a fine control over the iontronic response by easily modifying the applied potential.[41,42] The system presented here illustrates the potentiality of the combination of electroactive polymers and nanofluidic devices for achieving smart tuning of the

transmembrane current and the iontronic behavior using an easily controllable external parameter: the potential applied to the porous membrane. As the voltage-induced redox transformation of the polymer yields a variation of the surface charge density depending on the applied potential, by changing the applied potential, it is possible not only to modulate the nanochannel conductance but also to modify the iontronic behavior between ohmic and diode-like regimes at voltages above 0.6 V.[41,42,53] We hope the present results will inspire further studies involving the integration of redox polymers into solid-state nanofluidic devices as it emerges as a promising field to be explored.

ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.9b05961.

> Detailed experimental procedures (including estimation of tip diameter and statistical analysis) and electrochemical, ellipsometric, contact angle and scanning electron microscopy characterization (PDF)

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Notes

The authors declare no competing financial interest.

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