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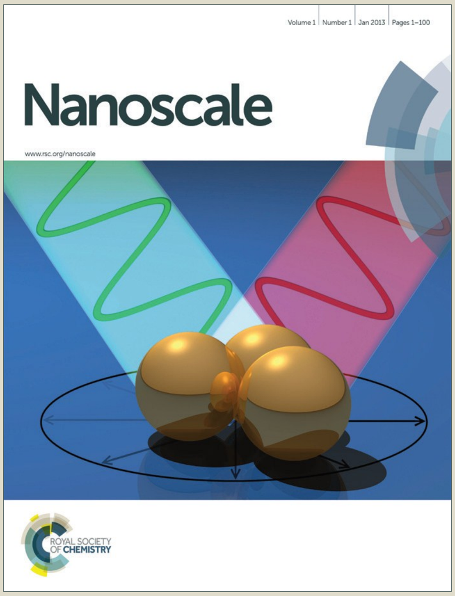

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Rectification of nanopores in aprotic solvents – Transport properties of nanopores with surface dipoles

Timothy Plett,[a] Wenqing Shi,[b] Yuhan Zeng,[b] William Mann,[a] Ivan Vlassiouk,[c]
Lane A. Baker,[b,*] Zuzanna S. Siwy[a,d,e,*]

[a] *Department of Physics and Astronomy, University of California, Irvine, CA 92697, United States*

[b] *Department of Chemistry, Indiana University, Bloomington, IN 47405-7102, United States*

[c] *Oak Ridge National Laboratory, Bethel Valley Road, Oak Ridge, TN, 37831, United States*

[d] *Department of Chemistry,* [e]*Department of Bioengineering, University of California, Irvine, CA 92697, United States*

Abstract

Nanopores have become a model system to understand transport properties at the nanoscale. We report experiments and modeling of ionic current in aprotic solvents with different dipole moments through conically shaped nanopores in a polycarbonate film and through glass nanopipettes. We focus on solutions of the salt $LiClO_4$, which is of great importance in modeling lithium based batteries. Results presented suggest ion current rectification observed results from two effects: (i) adsorption of Li^+ ions to the pore walls, and (ii) a finite dipole moment rendered by adsorbed solvent molecules. Properties of surfaces in various solvents were probed by means of scanning ion conductance microscopy, which confirmed existence of an effectively positive surface potential in aprotic solvents with high dipole moments.

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[*] Corresponding Authors: lanbaker@indiana.edu, Ph. (812) 856-1873; zsiwy@uci.edu, Ph. (949) 824-8290

Introduction

Synthetic nanopores have been subject of study for several decades, both through experiments and computer modeling.[1-5] A variety of methods have been used to fabricate single nanopores in different materials e.g., FIB[6] and TEM[7] drilling in silicon nitride, graphene,[8] and MoS_2 films[9], pulling of glass nanopipettes,[10,11] wet-etch in polymers,[12-18] controlled dielectric breakdown of silicon nitride,[19] even DNA folding[20,21] and carbon nanotubes[22-26]. Sub-nm tuning of the pore opening diameter has recently been reported via electrochemical reaction performed in single-layer MoS_2 films[27], and by inducing defect nucleation centers in graphene[28]. Electrolyte solutions used to probe ionic transport properties are almost always inorganic salts in water, and a rich collection of modeling and experimental data to predict and explain transport phenomena in nanopores in aqueous salt solutions now exists.[1,2] In a few exceptions, solvents like ionic liquids[29,30] and organic solvent/electrolyte systems[31] have been explored. Nanopores in nonaqueous solvents have exhibited phenomena that deviate from aqueous studies.

Among these phenomena, one of the most interesting effects observed with nanopores is the peculiar behavior of ionic current rectification. Rectification can be caused by asymmetry of the pore's geometry, e.g., the case of conically shaped nanopores, and the presence of surface charges.[5,10,13-18,32,33] Ionic concentrations in an asymmetric and charged nanopore are voltage-dependent; for one voltage polarity, concentration of both cations and anions exceed the values in the bulk, while for the opposite voltage polarity a depletion zone is created.[34-37] This effect has been confirmed for nanopores in a variety of materials that possess similar geometry and surface charge characteristics.[5] Ion current rectification has also been observed in geometrically symmetric nanopores with patterned surface charges where a junction between two zones with positive and negative surface charges exists.[38-44] A report has also been published showing rectification of currents carried by large organic ions in glass pipettes, and proposed that surface adsorbed electrolyte ions can cause effective charge inversion.[31]

Recently, discoveries have been made in the field of electrical energy storage, which utilize model nanostructures and architectures to increase energy storage and power density[45] in lithium ion battery technology. This has generated new interest and efforts toward understanding the transport properties of lithium at the nanoscale, and has led to new experiments with nanopores to address these queries. One reported series of experiments with conical nanopores in polyethylene terephthalate (PET) showed that rectification behavior was dependent on the cation used to probe the pore.[46] This was linked to the likelihood of the cation to 'dwell' near the charged surface of the pore wall, which caused modulation of the effective surface charge. As revealed by molecular dynamics simulations, a larger number of lithium ions stayed adsorbed close to the surface compared to sodium and potassium ions, which led to lowest rectification in lithium chloride. Recent work has also been done on lithium transport through nano-fabricated battery materials[47, 48] (manganese oxide), which revealed this cathode material, at various oxidation states, possesses nano-constrictions with excess surface charge. However, these experiments were conducted in aqueous solutions, which are not ideal or representative of lithium ion battery technology,[49] which relies on use of organic solvents to resist electrode degradation and improve capacity retention and cycle life.[50,51]

Here we propose a method utilizing two types of conical nanopores, conical nanopores in polycarbonate films[17] and conically shaped glass nanopipettes,[10,11,52,53] to compare the behavior between aqueous solutions and propylene carbonate (PC) solutions. PC is chosen as an organic solvent commonly used in lithium ion battery studies.[49] The intent is to examine the effect of nanoconstrictions on lithium transport in a solvent environment similar to that used in traditional battery experiments. We also seek to examine the effect of solvent on ion transport properties, which has heretofore not been closely studied. We chose to examine conical nanopores in polycarbonate, rather than polyethylene terephthalate used in previous studies,[13,46] due to stability of the polycarbonate pores in propylene carbonate. To widen the scope of examined organic solvents, experiments were also performed with glass nanopipettes. We postulate a new mechanism of ion current rectification via finite dipole moment of pore walls, which originates from solvent adsorption. Importance of polarizability of the nanopore material and induced dipoles for ionic current in nanopores has been modeled before.[54] This work provides experimental and modeling evidence of the importance of surface dipole moment rendered by the solvent.

Methods

Chemicals and Materials: Lithium perchlorate (99.0%, Sigma-Aldrich, St. Louis, MO) was dissolved in acetonitrile (ACN, distilled from 99.8%, Macron, Center Valley, PA), propylene carbonate (PC, distilled from 99.7% or dried over 5Å sieves for at least 24 hours, Sigma-Aldrich St. Louis, MO) and tetrahydrofuran (THF, 99.9%, Sigma-Aldrich St. Louis, MO). Resultant solutions were used as bath solution and to fill the nanopipettes. Polymer nanopores were studied in aqueous and PC solutions of $LiClO_4$, in 100 mM and 10 mM solutions of $NaClO_4$ (98.0%, Sigma Aldrich, St. Louis, MO), and in 10 mM-mass-equivalent KCl (99.0%, Macron, Center Valley, PA) solution in PC. Electrodes used in the current-voltage (I-V) measurements were AgCl coated Ag wires.

Preparation of conical polymer pores: Single conically shaped nanopores were prepared in 10 μm thick films of polycarbonate using the track-etching technique.[12] First, films were irradiated with single U ions accelerated to 11.4 MeV/u at the UNILAC linear accelerator of the GSI Helmholtzzentrum fur Schwerionenforschung in Darmstadt, Germany.[55] In the next step, irradiated films were subjected to wet chemical etching performed in a homemade conductivity cell. Etchant used was 8 M KOH with a 80/20 water/ethanol (v/v). This was done in compliance with a publication by Fujimoto et al. that established chemical bulk etching rates for two standard polycarbonate membranes, 1.69 and 1.78 μm/h for Lupilon and Makrofol foils respectively.[56] We estimated our chemical bulk etch rate to be an average of the two rates reported, yielding ~1.74 μm/h, or ~30 nm/min. We used these numbers to calculate the base and tip dimensions of our conical nanopores. Etchant was loaded into one side of the chamber and an acidic stopping medium in the other. This asymmetric etching procedure has been extensively studied and results in conically shaped nanopores.[13-16]

Characterization of conical nanopores via current-voltage recordings. A Keithley 6487 picoammeter/voltage source (Keithley Instruments, Cleveland, OH) was used to record all current-voltage curves, except for the case of scanning ion conductance microscopy (SICM) measurements. For both polymer and glass pores, Ag/AgCl electrodes were used to apply transpore voltages and to record currents. For all measurements here, the same electrolyte solution was utilized on each side of the pore. Electrical sizing of polymer nanopores was carried out after the pores exhibited stable current-voltage responses over the tested voltage window (-3 V to +3V) in 1 M KCl (aq). Two homemade Ag/AgCl electrodes were used to apply voltage and record current. The ‘tip’ of the nanopore was estimated based on the linear portion of the recording and approximating the pore shape as a truncated cone.[14] The large opening corresponded to the side in contact with the KOH and was estimated based on the bulk etch rate reported above. Diameters of pores used in this study were 4 –100 nm and 300 – 650 nm for small (tip) and large opening (base), respectively.

Preparation of conical glass nanopipettes: Quartz capillaries (Sutter Instruments, Novato, CA) with 1.0 mm outer diameter and 0.7 mm inner diameter were pulled with a P-2000 CO_2-laser pipet puller (Sutter Instruments, Novato, CA) to produce two symmetric sibling nanopipettes. Puller program parameters are as follows, heat: 690; filament: 3; velocity: 45; delay: 165, pull: 190. Scanning transmission electron microscopy (FE-SEM, FEI Quanta-FEG, Hillsboro, OR) was used to characterize the geometry of the obtained nanopipettes.

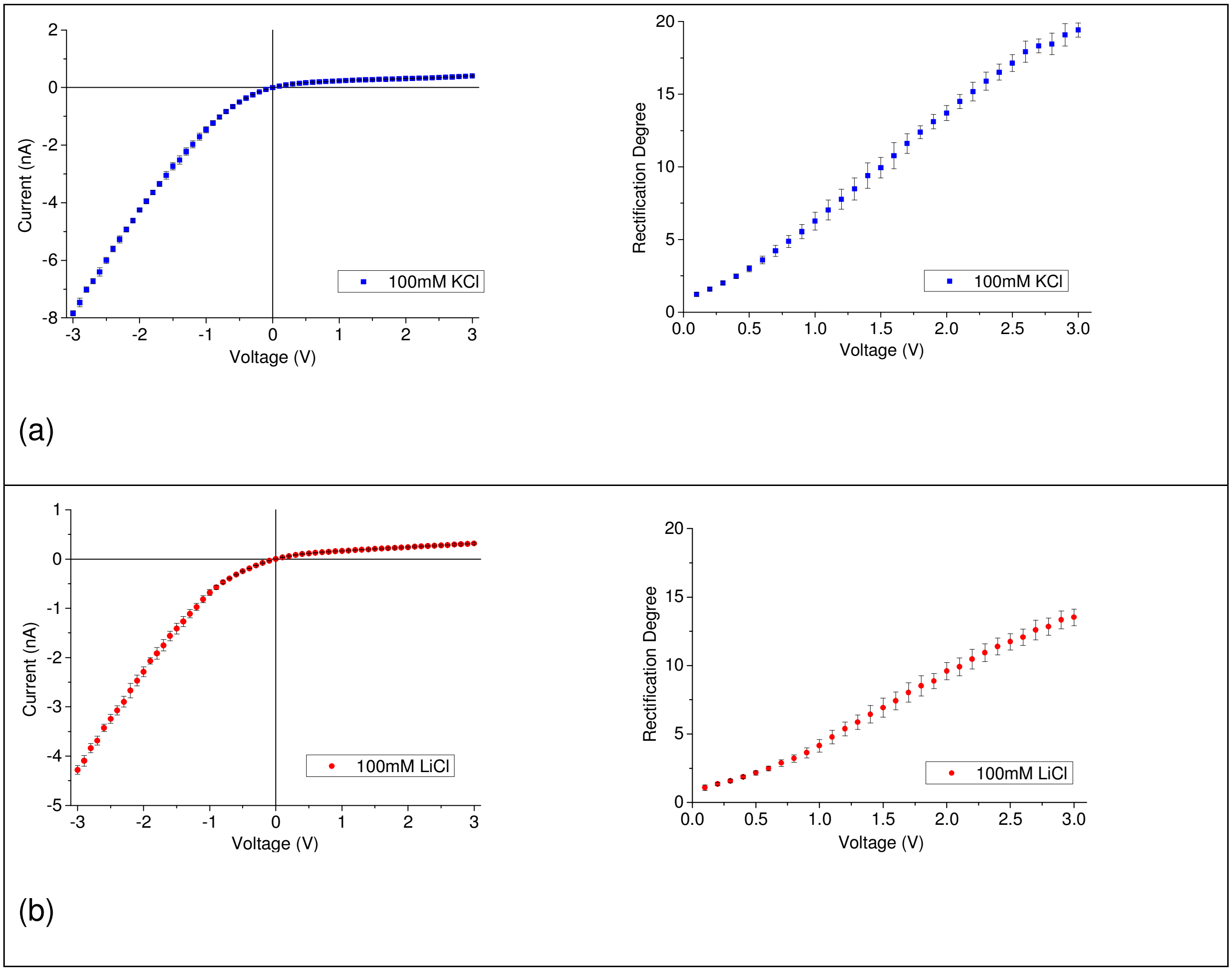
Surface charge investigations with SICM: In previous reports, we have demonstrated that as an asymmetric charged nanopipette is brought in close proximity to a surface of interest, surface charge of the substrate can influence ion transport in the gap between the nanopipettes tip and surface. This surface-induced effect was used to differentiate between surfaces that were positively or negatively charged.[52,53] Here, similar methods were employed to further understand the apparent surface charge behavior of polycarbonate membrane in PC. A current-voltage (I-V) curve was recorded when the nanopipette was far away from the substrate. The nanopipette was then moved towards the surface with a piezoelectric positioner (Park Systems XE-Bio SICM/AFM, Suwon, South Korea) until the probe was ~100 nm away from the substrate. A second I-V curve was then recorded and the two responses (far from the surface and near) were compared.

In experiments here, a polycarbonate membrane was immersed in 100 mM $LiClO_4$ in PC. Current-voltage curves were taken with two Ag/AgCl electrodes (one inside the nanopipette and one in the bath solution), over an applied potential range of -3 V to +3 V. For control experiments on polycarbonate membranes, 100 mM $LiClO_4$ in aqueous solution was used to fill nanopipettes and bath solution, and an applied potential range from -1 V to +1 V was used. Additional control experiments were carried out on glass substrates immersed in either PC or ACN solutions of $LiClO_4$.

Comsol modeling: Poisson-Nernst-Planck equations were solved using the Comsol Multiphysics 4.3 package.[57] A single 10 μm long conically shaped nanopore had opening diameters of 15 and 500 nm, respectively. The surface charge density of the pore walls was calculated as shown in Table 1. Fine triangular mesh of 0.5 nm was used close to the charged walls. In the remaining parts of modeled structures, mesh was reduced to the point when no change in the observed concentration profiles and currents was observed upon further mesh decrease. Dielectric constants were taken equal to 64, 37.5 and 7.58 for PC, ACN and THF, respectively. For simplicity, diffusion coefficients 2×10^{-9} m^2/s were used for both cations and anions in all solvents.

Results and Discussion

Figure 1 shows current-voltage curves of a single conically shaped polycarbonate nanopore with a narrow opening diameter of 10 nm, and a wide opening of 540 nm, recorded in aqueous solutions of three different monovalent salts. As expected and shown before in the literature, single conical nanopores in polycarbonate films behaved similarly to their polyethylene terephthalate (PET) counterparts, studied extensively by us[e.g.13,14,15,32] and other groups,[e.g.18,35,58] in that they showed ion current rectification (Figure 1).[5,17,32] Pores in these two polymer materials contain carboxyl groups which, in aqueous neutral and basic solutions, render the pores negatively charged. Current rectification results from this excess negative surface charge of the pore walls and the conical shape of the pores.[5,10,11,13,14,18,34,35,37] In aqueous solutions, ion current through single polycarbonate conically shaped nanopores examined here showed similar dependence on type of salt as reported before for PET nanopores.[46] Namely, magnitude of ion currents and rectification in KCl were consistently higher than values observed with LiCl or $LiClO_4$ (Figure 1). Lower rectification in lithium salts is attributed to ability of lithium ions to lower the effective surface charge of surfaces covered with carboxyl groups.[46]



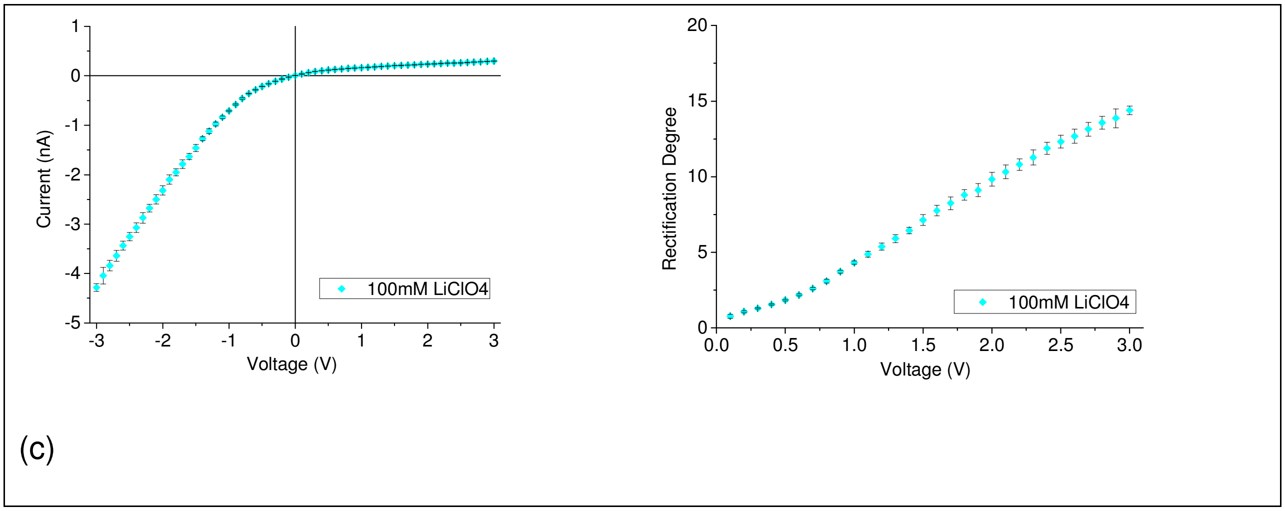
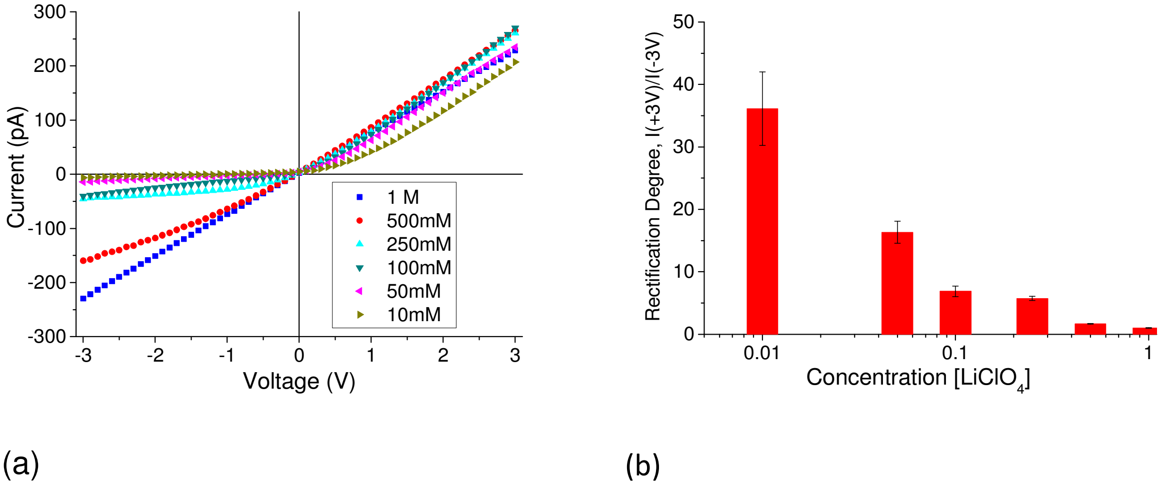


Figure 1. Current-voltage curves and rectification degrees recorded in a single polycarbonate nanopore with opening diameter of 10 nm (tip) and 540 nm (base). Recordings were made in aqueous solutions of (a) 100 mM KCl, (b), 100 mM LiCl (b), and (c) 100 mM LiClO$_4$. Rectification degree was calculated as a ratio of currents for negative and positive voltages.

In PC solutions however, a new, unexpected effect emerged. Because PC is protophobic in nature,[59] carboxyl groups on the pore walls are less likely to deprotonate since dissociated protons are difficult to solvate. Without deprotonation, carboxyl groups do not impart a net charge to the pore walls, a key prerequisite for rectification phenomenon observed in conical nanopores. For an uncharged conical nanopore, the predicted response with these solutions would be linear. However, in PC solutions tested here, conical nanopores (n=15) consistently exhibited rectification at low concentrations of salts. Further, rectification occurred in the opposite direction from that observed in aqueous solutions, i.e. with the same electrode configuration, positive currents were higher than negative currents. Figure 2 shows the effect in LiClO$_4$ solutions over a wide range of concentrations in a single nanopore with an opening diameter of 11 nm. Similar to experiments in aqueous solutions, a concentration dependence is observed, as well as tip size dependence in the response of a pore.[5,35] As tip size grew larger, the onset of this ‘reverse’ rectification occurred at lower concentrations (Figure S1 in Supporting Information). Note, inverted rectification was shown before for polymer pores in aqueous solutions only in cases when the pore walls carried excess positive surface charge.[5,18,39]

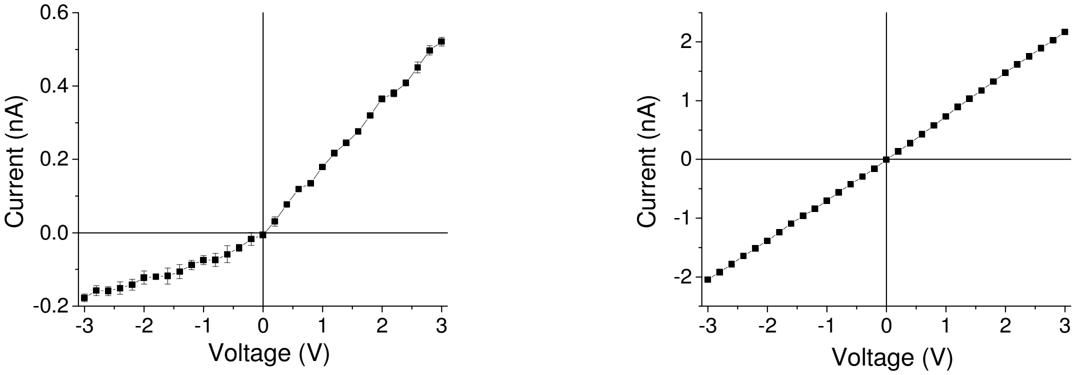
To test if the inverse rectification of current recorded with the simple inorganic salt of $LiClO_4$ could be observed in another conically shaped rectifying nanopore system, we also tested behavior of glass nanopipettes. In aqueous solutions, walls of glass pipettes are negatively charged due to deprotonation of silanol groups. Figure 3a shows current-voltage curves recorded in 10 mM $LiClO_4$ in PC. Similar to the recordings in polycarbonate pores (Figure 2), current-voltage curves recorded in PC are inverted compared to the measurements performed in the water solution.[10,11,31,36]

Of note, inverse current-voltage curves in glass nanopipettes have been reported previously for an organic electrolyte, tetraphenylarsonium tetraphenylborate (TPAsTPB), dissolved in a range of organic solvents.[31] Since large cations were reported to adsorb to surfaces,[60] adsorption of $TPAs^+$ to walls of glass pipettes was deemed responsible for creation of an effective positive surface charge,[33] which led to inverse rectification. Rectification of currents carried by TPAsTPB was reported for sub-mM concentrations of electrolyte, thus for conditions in which formation of ion-pairs was suppressed.



(a) (b)

Figure 2. (a) Current-voltage curves recorded in a range of $LiClO_4$ concentrations in propylene carbonate for a single conical polycarbonate nanopore with the tip opening of 11 nm and the wide opening of 470 nm. (b) Rectification degree calculated as a ratio of currents in +3V and -3V.

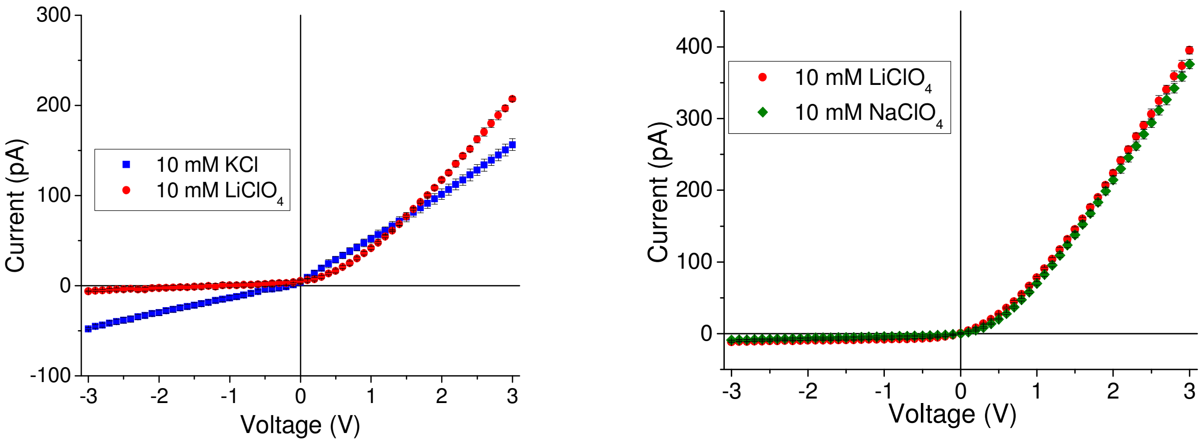


(a) (b)

Figure 3. Current-voltage curves recorded in (a) 10 mM and (b) 100 mM $LiClO_4$ in propylene carbonate through a glass nanopipette with an inner opening of 35 nm.

We propose two possible mechanisms, which could be the basis of the inverse rectification observed with the lithium inorganic salt in PC. The first, similar to the model presented by Yin et al.[31] and Cruz-Chu et al.,[33] considers the possibility of lithium ions adsorption to the polymer and glass surfaces, which could lead to an effective positive surface charge. The second mechanism focuses on the importance of the solvent, namely, if solvent adsorption could render a finite dipole moment at pore walls. [61,62]

To test these hypotheses, a series of experiments were conducted, each focused on a separate mechanism. Lithium ions in aqueous solutions have previously been found to adsorb to carboxyl groups.[46] Thus we considered if lithium ions in PC could show preferential binding to the pore walls as well. Since in PC we do not expect the carboxyl groups to be deprotonated, adsorption of lithium ions would lead to the formation of effectively positively charged pore walls. Experiments were also performed in $NaClO_4$ and KCl solutions in PC, because the tendency of Na^+ ions to bind to surfaces was reported to be weaker than of Li^+, and K^+ ions displayed almost no binding to carboxylated surfaces.[46] Figure 4 compares current-voltage curves recorded in 10mM $LiClO_4$, $NaClO_4$, and KCl solutions. This set of results demonstrates the presence of reverse rectification is not cation or anion dependent, although the rectification degree varied for the different salts. This further suggests ion current rectification observed in PC salt solutions does not arise solely from cation adsorption or charge inversion, although adsorption of lithium could be responsible for enhanced rectification in lithium salts. Due to limited solubility of KCl in PC, studies of a range of salt concentrations were not possible. Similarity between sodium and lithium perchlorate solutions may be explained by sodium also having a tendency to bind to polymer surfaces, though experiment and modeling predicted this to a significantly lesser degree than lithium.[40] Because the sodium salt has excellent solubility in PC, 100mM solutions of $LiClO_4$ and $NaClO_4$ were also compared, and similar concentration dependencies were observed (Figure S2 in Supporting Information).



(a) (b)

Figures 4. Current-voltage curves through a single polycarbonate nanopore with openings of (a) 10 nm (tip) and 470 nm (base) recorded in 10 mM KCl and 10 mM $LiClO_4$, and (b) 10 nm (tip) and 700 nm (base) recorded in 10 mM $LiClO_4$ and 10 mM $NaClO_4$ in propylene carbonate.

To explain the observed ion current rectification in PC, we also considered the possibility that pore walls in this solvent contain a positive dipole moment due to adsorption of PC molecules to the polymer surface. A previous study with TiO_2 surfaces in contact with PC, revealed that adsorption of PC occurs via the carbonyl oxygen, such that the carbon with positive partial charge pointed away from the surface.[62] In another set of experiments performed with thin films of $LiCoO_2$ in contact with PC, two preferential configurations for solvent adsorption were identified.[63] One configuration was similar to that identified for Ti_2O surfaces, while in the other, the carbonyl oxygen with partial negative charge pointed to solution. Propylene carbonate has a dipole moment of ~5 Debyes, (~2.7 times higher than the dipole moment of water), which might be strong enough to exert a significant effect on local ionic concentrations in a nanopore environment.

As shown in the literature developed for biological membranes, which often feature surface dipoles, even without net charge of the membrane, surface dipoles can cause formation of finite electrical potential in solution, to create an electrical double layer with modified local ionic concentrations.[64,65] The modeling predicted a complex surface with positive dipole moment and negative surface charge can behave as an effectively positive or negative surface depending on the relative dipole and surface charge densities. In the limit of low surface potentials, the equation for electric potential, φ, at a distance z from a wall containing surface charges of density, σ, and dipole density of, v, present within a layer of thickness, l, has the following form [65].

$$\varphi(z) = \frac{4\pi}{\varepsilon k}[\sigma cosh(kz) - vksinh(kz)]e^{-kl}, \text{ for } 0<z<l \qquad (1)$$

where k is the inverse Debye length and ε stands for dielectric constant.

For larger distances, $z>l$, the electric potential assumes the following form as a function of $(z\text{-}l)$:

$$\varphi(z-l) = \frac{4\pi}{\varepsilon k}[\sigma cosh(kl) + vksinh(kl)]e^{-kl}e^{-k(z-l)} \qquad (2)$$

So that the effective surface charge of the wall equals to:

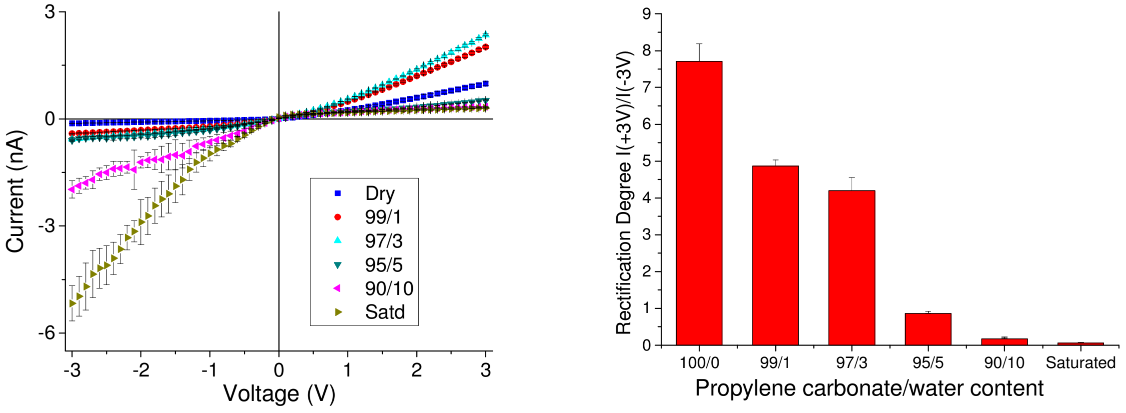
$$\sigma_{eff} = [\sigma cosh(kl) + vksinh(kl)]e^{-kl} \qquad (3)$$

suggesting, the electric potential indeed results from the density of surface charges and the density of surface dipoles. Note that in the absence of the polarizable layer, l=0, or dipole moment, v=0, σ_{eff} converges to the surface charge density, σ (cosh(0)=1), considered in the Poisson-Boltzmann approach without polarizability.

Equations (1-3) also explain the salt concentration dependence of ion current rectification shown in Figure 2. As the $LiClO_4$ increases, the electrical double-layer, k^{-1}, decreases, diminishing the surface potential, which is responsible for modulations of local ionic concentrations in the pore and ion current rectification.[32] Equation 3 also predicts that presence of dipoles with positive dipole moment, even when $\sigma=0$, is sufficient to render the surface potential positive; any possible adsorption of Li^+ (in the absence of carboxyl group deprotonation) would lead to finite and positive values of σ, further increasing the magnitude of potential. Moreover, addition of negative surface charges due to carboxylate groups is expected to reverse the direction of rectification to the behavior shown in Figure 1.

This theoretical approach does not consider polarizability of the membrane, because dipoles induced in the pore material were found to influence ionic current through nanopores primarily in cases where the product of the pore opening radius and inverse Debye length, $k \cdot r_{pore}$, was small, ~3.[54] In the considered here systems, e.g. in Figure 2, ion current rectification was observed even in 500 mM $LiClO_4$, thus with the pore radius of 5 nm, the product $k \cdot r_{pore}$ equals ~12. For the 35 nm in diameter glass pipette rectifying in 10 mM $LiCO_4$ (Figure 3a) $k \cdot r_{pore}$ is ~6.

Subsequent experiments were performed with solutions of gradually increasing ratios of water, which was expected to increase the number of deprotonated carboxyl groups. Example sets of recordings for two independently prepared nanopores are shown in Figure 5 and Figure S3. Experiments were performed with a standard solution of 100 mM $LiClO_4$ in a variety of PC/H_2O solutions: dry, 99/1, 97/3, 95/5, 90/10, and saturated. As reported before for the organic electrolyte TPAsTPB in glass pipettes,[31] water content had a direct impact on the rectification in a simple inorganic salt of $LiClO_4$ in polymer nanopores as well. For the pore shown in Figure 5, a threshold with ~5% water content when the recorded current-voltage curves are nearly linear is observed. With 10% water content by volume, the pore rectifies definitively in the same direction as in an aqueous conditions. An important point to note, however, is the inverted rectification in our system is present at water levels that are three orders of magnitude higher than in the system of TPAsTPB in glass nanopipettes (~1:10 vs. ~1:10,000).[31] We hypothesize the robustness observed here for inverted rectification with respect to the presence of water provides additional indirect evidence that rectification results from presence of a high density of dipoles caused by the adsorbed solvent.



(a) (b)

Figure 5 (a) Current-voltage curves recorded in 100mM $LiClO_4$ through a single polycarbonate pore with an opening of 60 nm (tip) and 440nm (base). The solutions were prepared in propylene carbonate with different levels (% by volume) of water content from 0% (dry propylene carbonate) to saturated water. With 5% water content the I-V curve was nearly linear marking indicating switching the direction of current rectification. (b) Rectification degree calculated based on data shown in (a) as I(+3V)/I(-3V).

To further elucidate the mechanism of ion current rectification in PC solutions of $LiClO_4$, experiments were performed in two additional organic solvents with lower dipole moments: acetonitrile (D=3.9) and tetrahydrofuran (D=1.7). Tests were done with glass pipettes due to their chemical stability in a wide range of chemical conditions. Figure 6 shows current-voltage curves of two 35 nm pipettes recorded in 10 mM $LiClO_4$ in ACN and THF. Notably, the pipettes exhibited similar, inverted rectification in the two organic solvents with high dipole moment (Figure 3a and Figure 6a), and ohmic behavior in THF (Figure 6b), which underscores the possible importance of the solvent dipole moment in the properties of ion transport through nanopores.

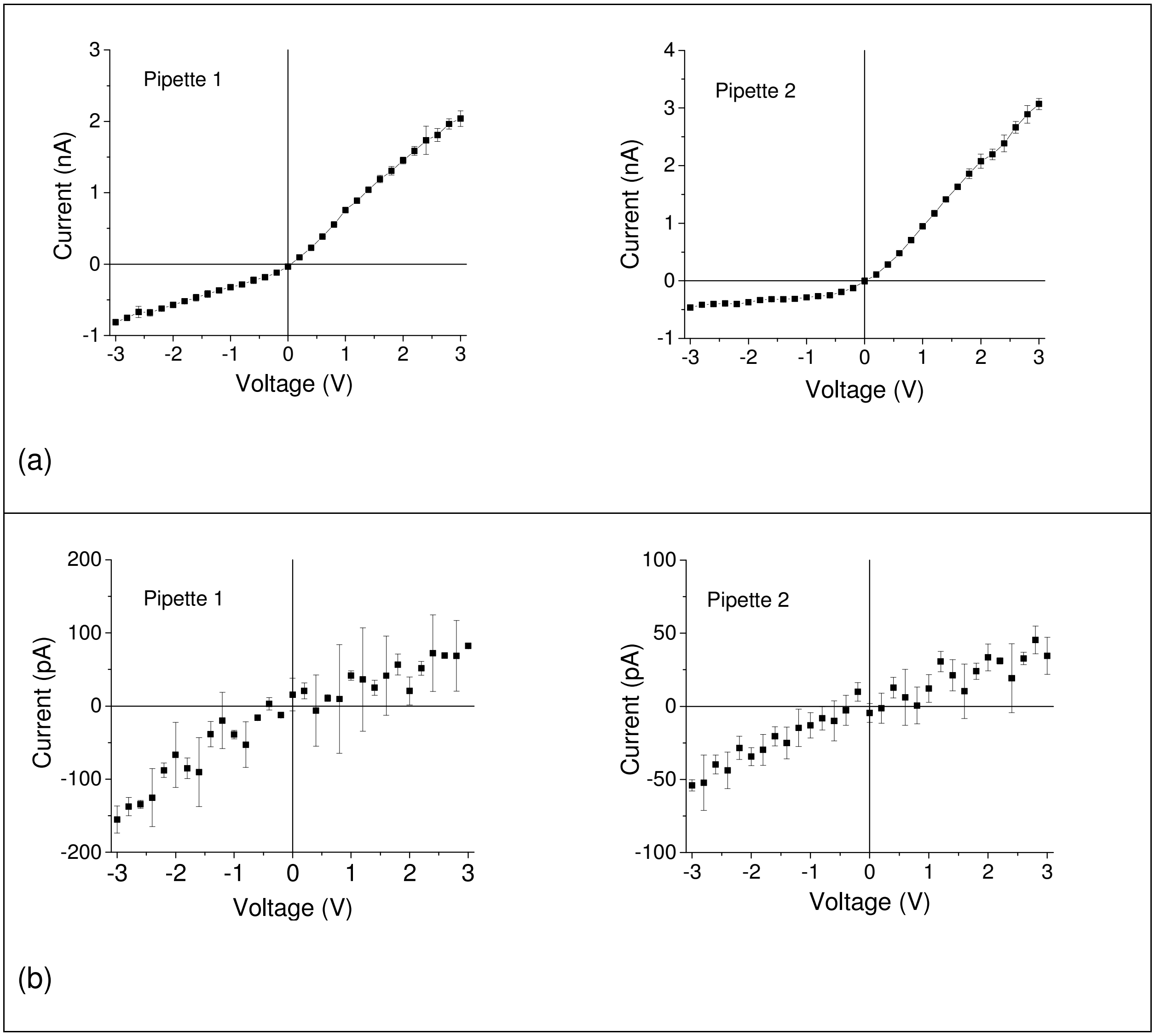


Figure 6. Current-voltage curves through two ~35 nm in in diameter glass nanopipettes recorded in 10 mM $LiClO_4$ in (a) acetonitrile, and (b) tetrahydrofuran.

Equation (3) indeed predicts the effective surface charge density due to the presence of dipoles will diminish with decrease of the dipole moment. Table 1 shows effective surface charge calculated for a flat surface in contact with 10 mM 1:1 salt in the three organic solvents, assuming solvent molecules are adsorbed at the density of three molecules per nm^2 in a configuration in which the partial positive charge faces the solution. The polarizable layer, l, was assumed to have a thickness of 2 nm due to the presence of surface roughness, and in case of track-etched polymer pores, dangling ends of the polymer chains.[66] Thus the layer containing dipoles is expected to be larger than the size of surface groups and solvent molecules. This is a simplified picture of our experimental system, but one that provides a qualitative argument for the possible existence of an effective positive charge in solvents with high dipole moment. Calculations also indicate that adsorption of positive ions can indeed have a large influence on the electrical properties of surfaces. As an example, adsorption of only one Li$^+$ per 20 nm^2 in THF increases the effective charge, σ_{eff}, nearly three times compared to the potential that originates from dipoles only, and becomes comparable to the magnitude of σ_{eff} in propylene carbonate without any cation adsorption. Since pores in THF do not rectify the current, we conclude that most probably the effect of dipoles dominates over the cation adsorption.

Table 1. Effective charge densities of a flat surface calculated from eq. (3)[64] for l=2 nm, assuming three solvent molecules are adsorbed per 1 nm^2. Three cases of additional surface charge originating from Li$^+$ adsorption were considered.

	Effective surface charge, σ_{eff}, calculated from eq. (3),[65] C/m^2		
Surface charge, σ, due to Li$^+$ adsorption, C/m^2	Propylene carbonate (D=4.9)	Acetonitrile (D=3.9)	Tetrahydrofuran (D=1.7)
0	0.0060	0.0048	0.0021
0.008 (1 per 20 nm^2)	0.01107 C/m^2	0.0098 C/m^2	0.0071 C/m^2
0.016 (1 per 10 nm^2)	0.0161 C/m^2	0.0149 C/m^2	0.0122 C/m^2

The presence of an effectively positive surface potential can also be measured experimentally via scanning ion conductance microscopy.[52,53, 67] The measurement consists of recording current-voltage curves when a glass nanopipette is in two positions, one far from the surface of interest and a second close to the surface (<100 nm). Experiments were performed in 100 mM LiClO$_4$, conditions at which the pipettes do not rectify in PC (Figure 3b). When the pipette is far away from the surface, only transport through the pipette is probed, and the local ionic concentrations at the pipette entrance are unaffected by the presence of a charged surface. When the pipette is held close to the surface, the measured ion transport is influenced by the constriction between the pipette and the surface as well as ionic concentrations perturbed by the surface charges; an asymmetric current-voltage curve provides evidence that the surface is charged.[52,53]

Figure 7 shows scanning ion conductance measurements for polymer and glass surfaces in aqueous and PC solutions of $LiClO_4$. Experiments confirmed the effective surface charge has an opposite sign in the two solutions. In PC, current-voltage curves exhibited higher positive currents, which, in our electrode configuration, indicate positive surface potential. Similar results were obtained in $LiClO_4$ solution in ACN (Figure S4 in Supporting Information). Measurements in THF could not be performed due to low signal-to-noise ratio in these conditions.

Taken together, our experiments in $LiClO_4$ and salt of other cations (see data for $LiClO_4$ and KCl in Figure 4) suggest the positive potential in PC and ACN results from both adsorption of Li^+ ions as well as solvent dipoles.

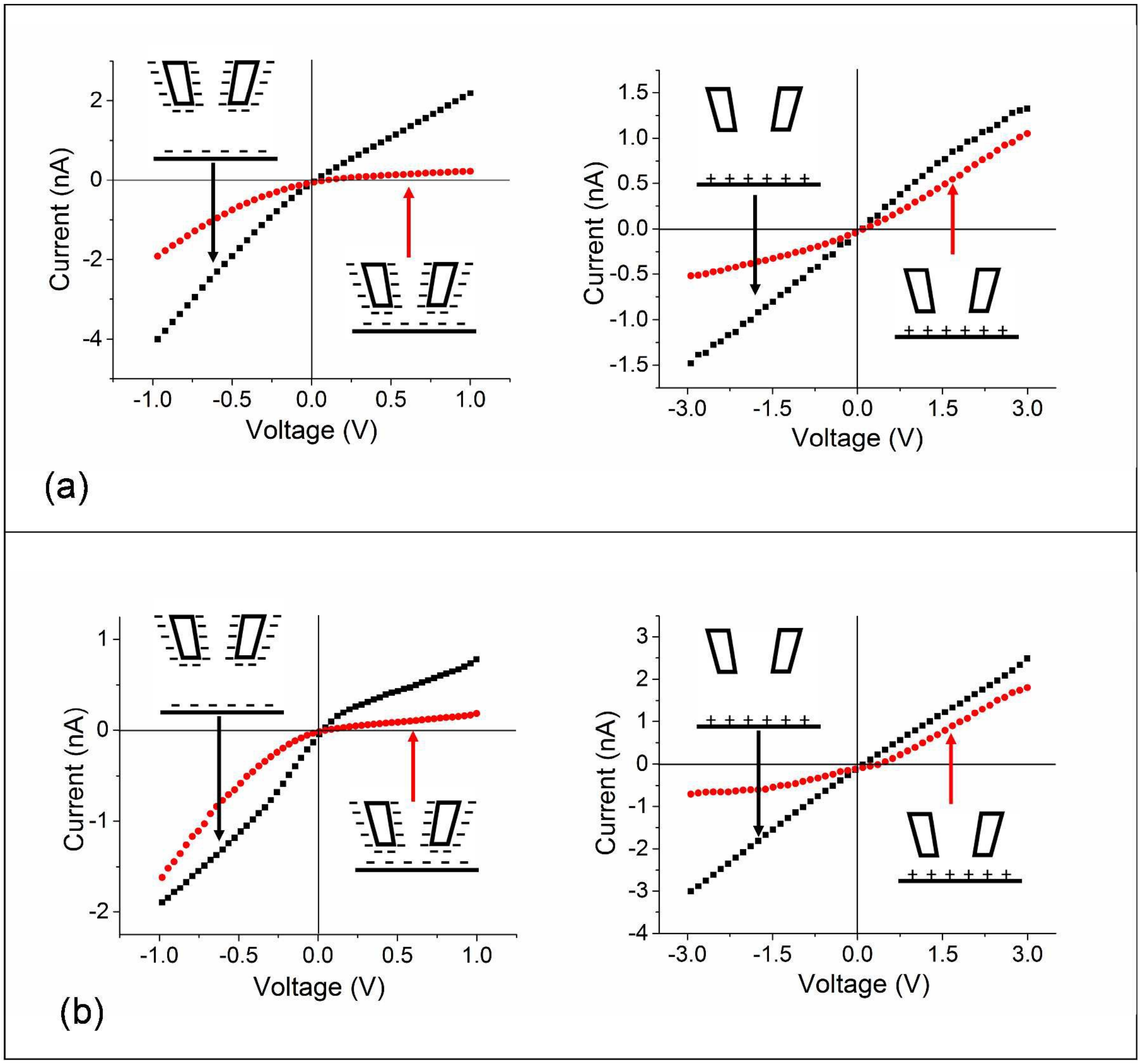


Figure 7. Scanning ion conductance measurements performed on (a) polycarbonate and (b) glass surfaces in aqueous (graphs on the left) and propylene carbonate (graphs on the right) solutions of $LiClO_4$. Insets present surface charge polarity on the glass pipette and on the surface examined.

Finally, we consider if the positive potential due to the possible presence of dipoles alone can induce ion current rectification in conically shaped nanopores. Comsol calculations were performed for a model system of a 10 μm long conical pore with opening diameters of 15 nm (tip) and 500 nm (base). We assumed 3 dipoles present per 1 nm^2 of pore walls for dielectrics equivalent to the three solvents studied here, with no adsorbed positive charge (i.e. no adsorbed lithium ions). The calculated current-voltage curves in 10 mM (Figure 8) are in a qualitative agreement with our experimental findings and predict a more ohmic behavior in THF. In order to perform quantitative modeling, information on diffusion coefficients of individual ions would have to be considered. Additional modeling aimed at understanding individual influence of dipole and cation adsorption will be performed in the future.

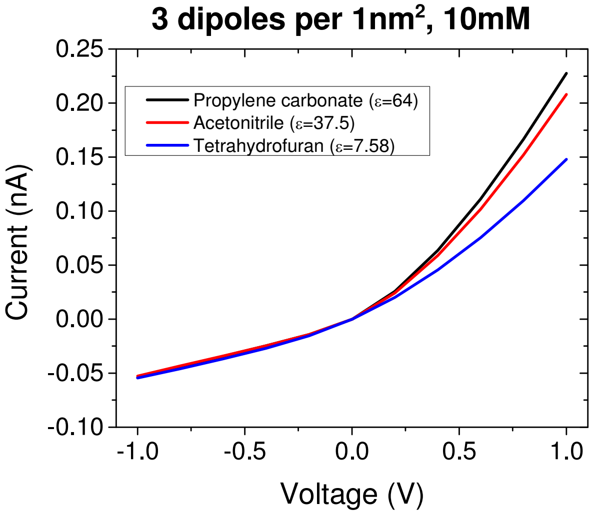


Figure 8. Numerical solutions of Poisson-Nernst-Planck equations predicting current-voltage curves through a single conical nanopore in 10 mM $LiClO_4$ in three organic solvents. The modeled nanopore had openings of 15 nm and 500 nm.

Conclusions

In this manuscript, we present an investigation of how solvent can influence ionic current and ion current rectification in conical nanopores. We focus on investigating solutions of $LiClO_4$ in propylene carbonate commonly used in lithium batteries. Two studied nanopore systems, pores in polycarbonate films and glass nanopipettes, showed inverted current-voltage curves in propylene carbonate compared to recordings in aqueous solutions. Inverted current-voltage curves in propylene carbonate suggest the existence of positive surface potential of the pore walls, further evidenced by measurements with SICM.

Rectification of conical pores in propylene carbonate solutions was explained by the interplay of two effects: (i) adsorption of Li^+ to the pore walls, and (ii) finite dipole moment of the pore walls rendered by adsorbed solvent molecules. The importance of surface dipoles on properties of biological membranes and channels has been known for a long time,[64,65] however, the effect of dipoles has not been considered yet for transport properties of man-made systems, with the exception of theoretical studies, which indeed predicted surface-dipole modified ionic concentrations in a nanopore, ion selectivity, and modification of rectification properties in cases when the thickness of the electrical double layer is comparable to the pore radius.[54,68] We expect that pores with dipoles might become the basis for the formation of new ionic devices controlling transport of ions, molecules, and water.

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