Electronic Supporting Information to:

Evaporation-driven electrokinetic energy conversion: critical review, parametric analysis and perspectives

Andriy Yaroshchuk[a,b]

[a]ICREA, pg. L.Companys 23, 08010, Barcelona, Spain

[b]Department of Chemical Engineering, Universitat Politècnica de Catalunya, av. Diagonal 647, 08028, Barcelona, Spain

Basics of electrokinetic phenomena in nanopores

Using the approach outlined in (Apel et al. 2021) and neglecting for simplicity salt-concentration gradients, from the transport equations derived in (Apel et al. 2021), we obtain this

$$J_v\left(\frac{1}{\chi}+\frac{\rho_{ek}^2}{g}\right)=-\nabla p+\frac{\rho_{ek}}{g}I \tag{S1}$$

$$-\nabla\varphi=\frac{I-\rho_{ek}\cdot J_v}{g} \tag{S2}$$

where J_v is the volume flux, p is the hydrostatic pressure, φ is the electrostatic potential, χ is the hydraulic permeability at zero voltage gradient,

$$\rho_{ek}\equiv F(Z_1\nu_1)\cdot c\cdot(\tau_1-\tau_2) \tag{S3}$$

is the electrokinetic charge density (the proportionality coefficient between electric-current density and volume flux under streaming-current conditions, i.e. $\nabla c=0, \nabla\varphi=0$)

$$g\equiv\frac{F^2}{RT}(Z_1\nu_1)c\left[Z_1\left(P_1-\frac{\omega}{\nu_2}\right)-Z_2\left(P_2-\frac{\omega}{\nu_1}\right)\right] \tag{S4}$$

is the electric conductivity at zero transmembrane volume flow, I is the electric-current density defined this way

$$I\equiv Z_1J_1+Z_2J_2 \tag{S5}$$

Within the scope of model of straight capillaries, the coefficients featuring in Eqs(S1-S4) can be expressed this way

$$P_i\equiv\langle D_i\Gamma_i\rangle+RTc_i\langle F[1]\rangle\left(\frac{\langle\Gamma_iF[\Gamma_i]\rangle}{\langle F[1]\rangle}-\tau_i^2\right) \tag{S6}$$

$$\omega\equiv RT\nu_1\nu_2c\langle F[1]\rangle\cdot\left(\frac{\langle\Gamma_1F[\Gamma_2]\rangle}{\langle F[1]\rangle}-\tau_1\tau_2\right) \tag{S7}$$

$$\tau_i\equiv\frac{\langle\Gamma_iF[1]\rangle}{\langle F[1]\rangle} \tag{S8}$$

where D_i are the ion diffusion coefficients, Γ_i are the ion partitioning coefficients, c is the virtual electrolyte concentration, $c_i \equiv \nu_i c$, ν_i are ion stoichiometric coefficients (they satisfy electroneutrality condition, $Z_1\nu_1 + Z_2\nu_2 = 0$), the brackets $\langle \quad \rangle$ mean averaging over the pore cross section, $\hat{F}[\quad]$ is a linear functional operator giving a solution to this equation

$$\eta \nabla^2 \vec{v} = -\vec{f} \tag{S9}$$

where $\vec{f}$ is an arbitrary function of coordinate inside the pore. The form of operator $\hat{F}[\quad]$ depends on the pore geometry. For example, in long straight cylindrical pores of equal size, all the flows are 1D, besides, the ion partitioning coefficients, Γ_i, depend only on the radial coordinate inside the pore. The operator can be shown to have this form (Yaroshchuk and Bondarenko 2018)

$$\hat{F}[\Gamma_i] = -\frac{r_p^2}{\eta}\left[ln(\rho)\int_0^\rho d\rho'\rho'\,\Gamma_i(\rho') + \int_\rho^1 d\rho'\rho' ln(\rho')\,\Gamma_i(\rho')\right] \tag{S10}$$

where η is the solution viscosity, r_p is the pore radius, ρ is the dimensionless radial coordinated scaled on the pore radius. The hydraulic permeability at zero voltage gradient in this case is equal to

$$\chi \equiv \langle F[1]\rangle = \frac{r_p^2}{8\eta} \tag{S11}$$

The ion transmission coefficients, τ_i, defined by Eq(S8) quantify the extent to which ions are convectively entrained by the volume flow. Notably, these coefficients are larger than one for counterions whose partitioning coefficients exceed unity. In principle, these coefficients can be affected by steric hindrance(Yaroshchuk et al. 2019) but this is not significant in nanopores whose size is much larger than the ion size (the focus of this study). Based on the same considerations, we also neglect the effect of steric hindrance on the ion diffusion and consider ion diffusion coefficients in nanopores constant and equal to those in bulk electrolyte solution.

Popular space-charge model postulates ion partitioning due to electrostatic interactions with fixed charges on the nanopore walls and local thermodynamic equilibrium (Yaroshchuk 2011). Accordingly, ion-partitioning coefficients can be obtained from the condition of constant electrochemical potential for each ion across the nanopore cross-section (Boltzmann distribution)

$$\Gamma_i = exp(-Z_i\psi) \tag{S12}$$

In combination with Poisson equation, this gives rise to Poisson-Boltzmann (PB) equation for the quasi-equilibrium dimensionless electrostatic potential, ψ

$$\nabla^2\psi = \frac{(\kappa r_p)^2}{Z_1 - Z_2}\left(exp(-Z_1\psi) - exp(-Z_2\psi)\right) \tag{S13}$$

where κ is the reciprocal Debye screening length defined as

$$\kappa \equiv \sqrt{\frac{2F^2 I_f}{\varepsilon\varepsilon_0 RT}} \tag{S14}$$

$$I_f \equiv \frac{1}{2}Z_1\nu_1(Z_1 - Z_2)\cdot c \tag{S15}$$

is the ionic strength in the virtual solution. For the cylindrical pore geometry, the boundary conditions are zero potential derivative at the pore axis (from the symmetry) and a given electric-charge density (potential derivative) at the capillary wall.

$$\left.\frac{d\psi}{d\rho}\right|_{\rho=1}=\frac{F\sigma r_p}{\varepsilon\varepsilon_0 RT} \qquad \text{(S16)}$$

where σ is the surface-charge density. One can also consider the so-called charge-regulation boundary condition (Israelachvili 2011). PB equation has several approximate solutions but they have limited applicability. Therefore, PB equation will be solved numerically. The integrations featuring in Eqs(S6-S8) will be performed numerically, too. See the ESI of (Yaroshchuk and Bondarenko 2018) for more detail on the procedures.

Nanopore conductivity (straight cylindrical nanopores, (1:1) electrolytes)

It has been shown that the second term in the right-hand side of Eq(S6) as well as the whole "mutual electro-diffusion" term given be Eq(S7) are very small in nanopores with well overlapped diffuse parts of electric double layers and are limited from above by 10-20% in broader nanopores (Yaroshchuk 1995). Therefore, for approximate estimates these terms can be neglected. Substituting the corresponding simplified version of Eq(S6) to Eq(S4), assuming constant diffusion coefficients, (1:1) electrolyte, performing cross-section averaging for cylindrical pore geometry, and using Eq(S12) for the ion-partitioning coefficients, we obtain

$$g=\frac{F^2c}{RT}\frac{2}{a^2}\int_0^a\left(D_+exp\left(-\frac{F\psi}{RT}\right)+D_-exp\left(\frac{F\psi}{RT}\right)\right)rdr \qquad \text{(S17)}$$

Estimates of streaming potential and EK-conversion efficiency for nanoporous films with pore size and surface charge mimicking polymer track-etched membranes

The surface-charge density in nanopores (24 nm diameter) of poly-ethylene-terephtalate track-etched membranes has recently been determined from simultaneous measurements of osmotic pressure and salt diffusion in KCl and LiCl solutions (Apel et al. 2021). For the surface-charge densities fitted to experimental data in this study (and identical cylindrical pores of 24-nm diameter), one calculate numerically (using the procedures described in (Yaroshchuk and Bondarenko 2018)) the electrokinetic-charge density, electric conductivity and hydraulic permeability at zero current (inverse of coefficient by volume flux in Eq(S1)) as well as streaming potential at maximum capillary pressure at complete wetting (ca.1.2 MPa) and EK-conversion efficiency for the side-evaporation configuration. The results are listed in Table S1. The calculations assumed the real porosity of track-etched membranes (ca.3.6%) but from the definitions of streaming-potential coefficient (Eq(43)) and EK-conversion efficiency (Eq(9)) one can see that these properties are independent of porosity because electrokinetic-charge density is independent of porosity (see Eq(S3)) while both hydraulic permeability and electric conductivity in the definition of EK-conversion efficiency are directly proportional to it.

Table S1. Streaming potential and EK-conversion efficiency in nanoporous materials mimicking electro-surface properties of track-etched membranes studied in (Apel et al. 2021)

Salt/ concentration	surface-charge	electrokinetic-charge	electric conductivity (mS/m)	hydraulic permeability $(nm/(s\cdot MPa))$	streaming potential (V)	electrokinetic-conversion

	density $(mA \cdot s/m^2)$	density $(A \cdot s/dm^3)$				efficiency $(16\Theta/27)$ (-)
KCl, 1.5 mM	-5.7	-73	2.8	0.64	-1.9	0.018
KCl, 3 mM	-9.5	-107	4.9	0.62	-1.6	0.022
LiCl, 1.5 mM	-5.6	-72	1.4	0.58	-3.4	0.031
LiCl, 3 mM	-9.3	-106	2.5	0.55	-2.7	0.036

Remarkably, while the streaming potential decreases with electrolyte concentration, the EK-conversion efficiency even somewhat increases. This is due to the considerable increase of surface-charge (and electrokinetic-charge) density with the electrolyte concentration.

Electrokinetics with electron-conducting substrates

In this section, we make an attempt of taking into account electron/hole conductance of matrix of nanoporous materials experiencing electrokinetic phenomena (streaming potential). We consider the simplest limiting case of sufficiently large pores without any appreciable overlap of diffuse parts of electric double layers.

Pressure-driven mode

In this section, we consider long straight channels with a pressure-drive flow. According to Eqs(4,7),

$$\frac{d\varphi}{dx} = \frac{\varepsilon\varepsilon_0}{\eta g}(\zeta - \bar{\psi})\frac{dP}{dx} \tag{S18}$$

In sufficiently broad channels, the average electrostatic potential, $\bar{\psi}$, is very small and can be neglected. Therefore, from Eq(S18), we obtain

$$d\varphi = \frac{\varepsilon\varepsilon_0\zeta}{\eta g}dP \tag{S19}$$

Here, φ is the electrostatic potential in the central part of the channel far away from its surfaces. Besides it, close to the surfaces there is a potential drop within diffuse part of electric double layer (zeta-potential). With electron-conducting substrates, the electrostatic potential of conductor surface must be the same all the way along the channel. In particular, this surface potential occurs at zero volume flow due to preferential adsorption of ions of one sign on the surface (or dissociation of ionogenic groups). Let us denote this constant surface potential ζ_0, so

$$\zeta + \varphi = \zeta_0 \tag{S20}$$

By substituting Eq(S20) to Eq(S19), we obtain

$$\frac{d\varphi}{\zeta_0 - \varphi} = \alpha dP \tag{S21}$$

where we have denoted

$$\alpha \equiv \frac{\varepsilon\varepsilon_0}{\eta g} \tag{S22}$$

In this simple analysis, we neglect the influence of electrokinetic phenomena on the volume flow (this is justified just in sufficiently broad channels). Therefore, the hydrostatic pressure is independent of electrostatic potential and its profile is linear. Accordingly, Eq(S21) can be easily integrated along the channel to yield

$$\alpha\Delta P = ln\left(\frac{\zeta_0-\varphi(L)}{\zeta_0-\varphi(0)}\right) \tag{S23}$$

where L is the channel length,

$$\Delta P \equiv P(0) - P(L) \tag{S24}$$

is the hydrostatic-pressure difference along the channel. From Eqs(S23, S24) we obtain

$$\Delta\varphi \equiv \varphi(0) - \varphi(L) = \left(\zeta_0 - \varphi(0)\right)(exp(\alpha\Delta P) - 1) \tag{S25}$$

The hydrostatic-pressure profile is linear

$$P(x) = P(0) - \frac{\Delta P}{L}x \tag{S26}$$

Taking this into account, from Eq(S21), we obtain

$$\varphi(x) - \varphi(0) = \left(\zeta_0 - \varphi(0)\right)\left(1 - exp\left(\alpha\Delta P\frac{x}{L}\right)\right) \tag{S27}$$

One can see that, in contrast to the classical case of dielectric substrates, the electrostatic-potential profile is non-linear. The extent of non-linearity is controlled by the value of parameter $\alpha\Delta P$. Notably, when this parameter is small, we recover the same linear potential profile as in the classical case.

Physically, the constancy of surface electrostatic potential is ensured due to the appearance of polarization electron charges at the channel surfaces. Together with the initially present fixed charges (arising due to preferential ion adsorption or dissociation of ionogenic groups) they give rise to a position-dependent zeta-potential that can be found from the condition of constancy of surface electrostatic potential (Eq(S20)) and distribution of electrostatic potential outside the EDLs (Eq(S27))

$$\zeta(\xi) \equiv \zeta_0 - \varphi(\xi) \equiv \left(\zeta_0 - \varphi(0)\right)exp(\alpha\Delta P\xi) \tag{S28}$$

where $\xi \equiv x/L$ is the dimensionless coordinate scaled on the cannel length. We consider the conductor ungrounded. Therefore, the total induced electron charge is zero. There is this well-known relationship between surface-charge density and equilibrium electrostatic potential at a charged surface (Gouy-Chapman formula)

$$\sigma = 2\sqrt{2RT\varepsilon\varepsilon_0 c} \cdot sinh\left(\frac{\zeta}{2}\right) \tag{S29}$$

The surface-charge density is proportional to the hyperbolic sinus of zeta-potential. Taking into account this and the fact that the total surface charge under flow conditions must be equal to the charge at no flow, we obtain

$$sinh\left(\frac{\zeta_0}{2}\right) = \int_0^{L1} sinh\left(\frac{\zeta(\xi)}{2}\right)d\xi \tag{S30}$$

Substituting Eq(S28) for the distribution of zeta-potential, we obtain

$$sinh\left(\frac{\zeta_0}{2}\right) = \int_0^1 sinh\left(\left(\frac{\zeta_0 - \varphi(0)}{2}\right) exp(\alpha\Delta P\xi\ )\right) d\xi \tag{S31}$$

The integral in the right-hand side of Eq(S31) can be taken in terms of special functions

$$A \cdot sinh\left(\frac{\zeta_0}{2}\right) = Shi\left(\left(\frac{\zeta_0 - \varphi(0)}{2}\right) e^A\right) - Shi\left(\frac{\zeta_0 - \varphi(0)}{2}\right) \tag{S32}$$

where Shi is the integral hyperbolic sinus, and we have denoted

$$A \equiv \alpha\Delta P \tag{S33}$$

Eq(S32) is a transcendental equation for the determination of "entrance" electrostatic potential, $\varphi(0)$, as a function of parameter A, which is proportional to the hydrostatic-pressure drop along the channel. Given that integral hyperbolic sinus is a strongly increasing function of its argument, Eq(S32) shows that when parameter A increases, $\zeta_0 - \varphi(0) \to 0$. Physically, this means that the polarization charge distributes itself in such a way that the net charge density (fixed plus induced charge) at the channel "entrance" tends to zero whereas it "peaks" exponentially ever stronger (with increasing pressure difference) close to the "exit" (see Eq(S28)). Fig.S1 shows that for conducting substrates the dependence of streaming potential on applied pressure is essentially sublinear. This can be a problem in view of achieving sufficiently high streaming potentials in energy harvesting from evaporation.

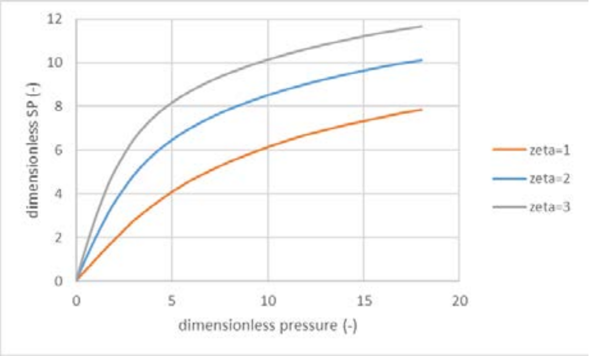

Fig.S1.Dimensionless OCV (streaming potential) as a function of dimensionless hydrostatic-pressure difference (parameter A defined by Eq(S33)); the values of "equilibrium" dimensionless zeta-potential (ζ_0) are indicated in the legend.

Evaporation-driven mode

We consider the system with side evaporation schematically shown in Fig.7. In this case, Eq(S18) is still applicable but the hydrostatic-pressure gradient is not constant but is given by Eq(30). Therefore, by assuming $\bar{\psi} = 0$ and using Eq(S20), we obtain

$$\frac{d\varphi}{\zeta_0 - \varphi} = \frac{\alpha q_e}{\chi h}(x - L)dx \tag{S34}$$

This can be easily integrated to yield

$$-ln\left(\frac{\zeta_0 - \varphi(x)}{\zeta_0 - \varphi(0)}\right) = \frac{\alpha q_e}{\chi h} x \left(\frac{x}{2} - L\right) \tag{S35}$$

$$\varphi(\xi) - \varphi(0) = \left(\zeta_0 - \varphi(0)\right)\left(1 - exp\left(\beta\xi\left(1 - \frac{\xi}{2}\right)\right) 1\right) \qquad \text{(S36)}$$

where $\xi \equiv x/L$ is the dimensionless coordinate along the porous film,

$$\beta \equiv \frac{\varepsilon\varepsilon_0}{\eta g}\frac{q_e L^2}{\chi h} \qquad \text{(S37)}$$

The local zeta-potential, $\zeta(\xi) \equiv \zeta_0 - \varphi(\xi)$, is

$$\zeta(\xi) = \left(\zeta_0 - \varphi(0)\right) exp\left(\beta\xi\left(1 - \frac{\xi}{2}\right)\right) \qquad \text{(S38)}$$

Taking into account as previously that the total induced electric charge should be zero and using Eq(S29), we obtain.

$$sinh\left(\frac{\zeta_0}{2}\right) = \int_0^1 sinh\left(\left(\frac{\zeta_0 - \varphi(0)}{2}\right) exp\left(\beta\xi\left(1 - \frac{\xi}{2}\right)\right)\right) d\xi \qquad \text{(S39)}$$

From this transcendental equation, one can find $\varphi(0)$ as a function of β. From Eq(S36) we obtain this expression for the coordinate dependence of derivative of electrostatic potential

$$\frac{d\varphi}{d\xi} = -\left(\zeta_0 - \varphi(0)\right)\beta(1 - \xi) exp\left(\beta\xi\left(1 - \frac{\xi}{2}\right)\right) \qquad \text{(S40)}$$

Fig.S2 shows an example of distribution of electrostatic-potential derivative.

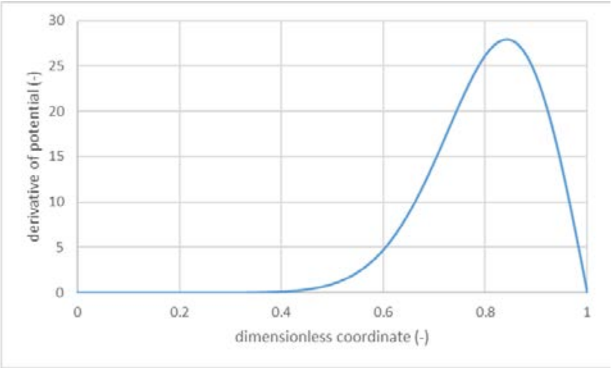

Fig.S2. Distribution of derivative of dimensionless OCV (streaming potential) with respect to dimensionless coordinate along porous film calculated using Eq(S40): $\zeta_0 = -3$, $\beta = 40$

This distribution is in qualitative agreement with experimental data obtained in (Xue et al. 2017) for nanoporous films made from carbon-black nanoparticles.