Efficiency of electrochemical gas compression, pumping and power generation in membranes

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ABSTRACT

The electrokinetic effects in membranes and porous materials can be used for direct conversion of pressure into electricity or conversion of electricity into pumping power, and they have potential applications within actuators, small scale pumping and energy harvesting devices. Still, in the literature only electrokinetic effects with liquid reservoirs on each side of the membrane are considered. In the present paper, isothermal electrokinetic effects are investigated using non-equilibrium thermodynamics in the case with gas phase reservoirs on each side of the membrane. For comparison the case with liquid reservoirs is included. We describe how the figure-of-merit, energy conversion efficiency, power density, compressor and generator curves depend on observable transport properties. The derived equations are used to analyse two examples with gas phase reservoirs. The first being related to electrochemical hydrogen compression/liquefaction, and the second being the electrochemical gas compression for cooling cycles. In the latter case, experimental transport data predict high efficiency and a power density which is promising with respect to membrane-based electrochemical cooling applications.

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1. Introduction

Electrokinetic effects in porous materials and membranes arise due to the coupling between the movement of ions and solvent. In e.g. water such a coupling can be explained and modelled by electrostatic interactions between charged ions and polar water molecules. Electrokinetic effects can be utilised for direct conversion of potential or kinetic energy (e.g. Pressurised liquids and gases) into electrochemical energy or vice versa [1]. This is potentially attractive for many applications [2] such as microfluidic pumps, gas compressors for cooling cycles, small generators in e.g. domestic compressed air energy storage [3] or heat engines e.g. organic Rankine cycles [4].

The Saxèn relations have been known since long, but specific studies of electrokinetic energy conversion were done first in the 1960s by Osterle and co-workers [1,5] and Burgreen and Nakache [6,7]. They predicted a maximum first law efficiency (η_{EK}) of the order 1–3% and up to 17%, respectively. During the past decade renewed interest in this topic has emerged; and most reports focus on the transport properties of straight nanochannels with well-defined dimensions [8–23]. Recently [2,24], experimental

values of the elecktrokinetic figure-of-merit [1,2,24] have shown that efficiency of about 20% can be obtained in commercial Nafion membranes and it is increasing with temperature.

Up to now all theoretical studies of electrokinetic energy conversion have only considered incompressible fluids and in particular aqueous solutions. However, gas phase electrokinetic energy conversion is possible too and the potential applications are electrochemical gas compression or power generation (expander). Some experimental works have been reported on electrochemical compression of H_2 through a membrane [25–29], with focus on high pressure liquefaction of H_2. Electrochemical gas compression in membranes for cooling applications is described in the patent literature, e.g. Refs. [30–32]. None of the patents disclose technical details or theoretical considerations with respect to e.g. efficiency and power density.

Fig. 1 gives a schematic illustration of electro-osmosis with liquid (left) and gas reservoirs (right). In the first case, an ion, say Li^+, migrates through the membrane due to an external electric potential (ϕ) difference. Each Li^+ couples with a number of water molecules, that are quantified by the water transport number (t_w). In popular terms one may say that Li^+ is dragging or pumping water through the membrane as it is moving in the electric field.

Alternatively, a gas phase can supply the conducting ion by gas oxidation and subsequent reduction on the two membrane sides.
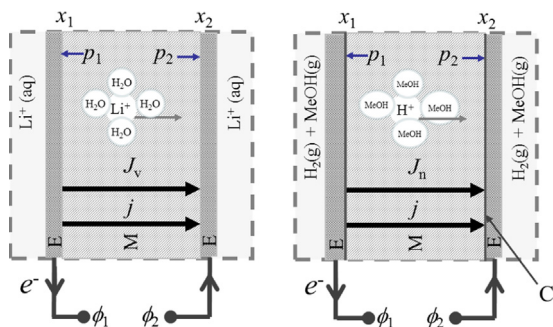
Fig. 1. Schematic representation of electrokinetic pumping (left) and gas compression (right) across a membrane (M) having thickness $\Delta x = x_2 - x_1$. Electrodes (E) generate an external electrical potential difference ($\Delta\phi = \phi_2 - \phi_1$) across the membrane that results in an ion current density (j) through the membrane. In the liquid phase a volume flux (J_v) and in the vapour phase a gas flux (J_n) arises due the coupling between the ion and the solvent. During operation a pressure difference ($\Delta p = p_2 - p_1$) between the two sides is present. In a practical system the pump could be designed similar to that of a redox flow battery where faradaic processes takes place in the whole volume of the porous (e.g. carbon felt) electrode. The compressor could be designed similar to that of a fuel cell with a membrane electrode assembly. Here the faradaic processes only take place in the catalyst layer (C) between the membrane surface and the electrode (electrically conductive gas diffusion layer).

The membrane surface is then covered with an electrode/catalyst. Examples of such gas reactions are $1/2\,H_2 \leftrightarrows H^+ + e^-$, $1/2\,Br_2 + e^- \leftrightarrows Br^-$ or $1/2\,Cl_2 + e^- \leftrightarrows Cl^-$. Other gas molecules, e.g. water, methanol or ammonia, in the gas phase can dissolve in the membrane and be transported along with the ion. This is quantified by the gas transport number (t_n) and in cooling cycles, this transported fluid acts as a refrigerant. Since electrokinetic pumping/compression with liquid or gas reservoirs are reversible processes an external pressure difference can be converted into an electrical power.

The basic theoretical description [1,5] of electrokinetic energy conversion is obtained from non-equilibrium thermodynamics. The theory has been used to find a general expression for maximum efficiency that increases with the electrokinetic figure-of-merit ($\beta = (\nu^2\sigma)/\kappa_H$), where ν is the streaming potential coefficient, σ is the ion conductivity and κ_H is the hydraulic permeability of the membrane [1,5]. One of the aims of the present article is to explore this theory in more details. In particular, we want to define pump and generator curves, and find requirements for maximum efficiency, power density, maximum pressure (pump head) etc. These parameters are very important for assessing electrokinetic energy conversion with respect to various applications.

Still, the major aim of the current article is to formulate the transport equations for the gas phase in a practically useful way. The theory of non-equilibrium thermodynamics is indispensable when it comes to correctly define the coupling phenomena, which are central in electrokinetic energy conversion. This includes the derivation of a general figure-of-merit and maximum efficiency along with other important parameters e.g. compressor and generator (expander) curves, requirements for maximum efficiency, power density, maximum pressure etc. Despite applications within the field of electrokinetic H_2 compression and the many patent applications for electrochemical cooling cycles, a theoretical basis has not yet been reported in the literature.

The following two theoretical sections cover electrokinetic energy conversion with liquid and gas phase reservoirs, respectively, and can be read independently. They are followed by a section that discusses the significance of the results along with estimates of efficiency of electrochemical gas compression based on transport data from the literature. The theory does not include effects from mass transport and catalytic activity in electrodes and electrode membrane interface. It can however

be included emperically as overpotentials as will be done later in the discussion.

2. Electrokinetic energy conversion with liquid phase reservoirs

2.1. Transport equations

Fig. 2 shows a circuit diagram of electrokinetic energy conversion. The central unit is a membrane, characterised by the ion conductivity (σ) and hydraulic permeability (κ_H). Electric power can be generated (Fig. 2 left) when a pressure difference ($\Delta p = p_2 - p_1$) is applied across the membrane, resulting in a volume flux (J_v) through the membrane. Due to the coupling between the movement of solvent and ions an electric current density (j) and a potential difference ($\Delta\phi = \phi_2 - \phi_1$) are induced in the electrical circuit, where electrical power can do work in an variable external load (R_L). In the pumping operation (Fig. 2 right), an electric potential difference across the membrane induces a current density along with a volume flow and a pressure difference arises across the membrane. The hydraulic work can be dissipated within a variable hydraulic load/resistance (R_L).

An isothermal system, at a fixed temperature T, exposed to an electric and a mechanical driving force obeys the following phenomenological transport Eqs. [1,5,33,34].

$$J_v = L_{vv}\left(-\frac{1}{T}\frac{\Delta p}{\Delta x}\right) + L_{v\phi}\left(-\frac{1}{T}\frac{\Delta\phi}{\Delta x}\right) \tag{1}$$

$$j = L_{\phi v}\left(-\frac{1}{T}\frac{\Delta p}{\Delta x}\right) + L_{\phi\phi}\left(-\frac{1}{T}\frac{\Delta\phi}{\Delta x}\right) \tag{2}$$

The direction and magnitude of the volume flux (J_v) and current density (j) is determined by the transport coefficients (L_{ij}) where the off-diagonal coefficients (written with appropriate units) obey the Onsager relation $L_{v\phi} = L_{\phi v}$.

In the following, the phenomenological transport coefficients are related to observable transport coefficients. The electric
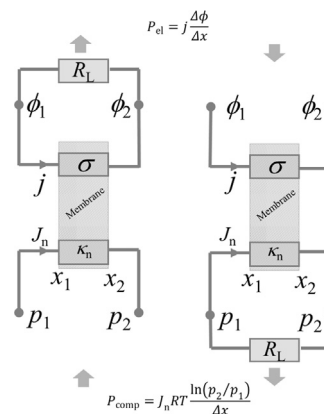
Fig. 2. Diagram of electrokinetic power generation/expander (left) and compression (right) across a membrane. The system is charachterised by an ion conductivity (σ), electrical current density (j), gas permeability (κ_n) and gas flux (J_n). During power generation (left) the pressure difference ($\Delta p = p_2 - p_1$) is negative and the potential difference ($\Delta\phi = \phi_2 - \phi_1$) is positive. For compression the signs are reversed. With this convention j and J_n are always positive. The streaming potential coefficient (not shown in figure) is negative for cation conductive membranes and postive for anion conductive membranes. The arrows at the top and bottom indicate wheter electric power (P_{el}) or compression/expansion work (P_{comp}) is inserted to or extracted from the system. The case for liquids reservoirs on each side is fully equivalent, here κ_n and J_n are replaced with the hydraulic permeability (κ_H) and volume flux (J_v), respectively. While P_{comp} is replaced with the hydraulic power ($P_{hyd} = J_v(\Delta p/\Delta x)$).