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PECULIARITIES OF ION TRANSPORT IN AQUEOUS ELECTROLYTES CONFINED IN ANODIC ALUMINA (AAO) NANOCHANNELS

translate
waste heat to electricity

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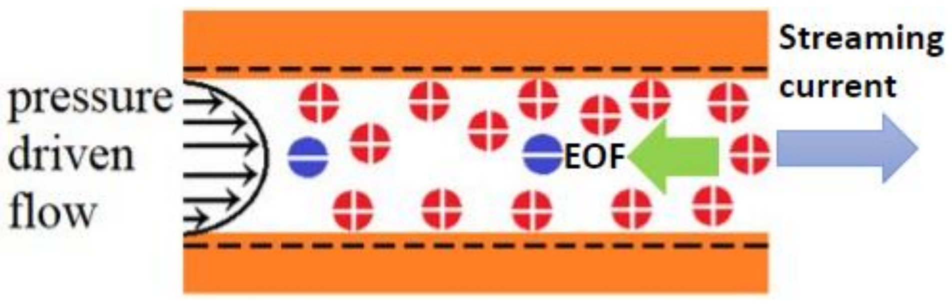
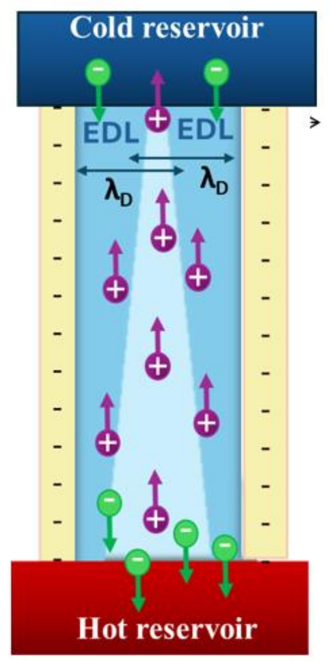
INTRODUCTION

Nanofluidics has received increasing attention in the field of energy conversion in recent years. Various unique ion transport properties within nanochannels, including selective ion transport, ion current rectification, and ion concentration polarization, have been exploited **to develop energy-harvesting devices**.
The ion transport can be caused by various driving forces:
- ✓ external pressure gradients;
- ✓ electrostatic forces;
- ✓ temperature;
- ✓ concentration gradients.

***Thus, understanding the transport behaviour of electrolyte solution through nanochannels is crucial to increasing energy-conversion efficiency*.**



Schematic representation of the different electrokinetic effects occurring in nanochannel when electric double layer (EDL) overlapping

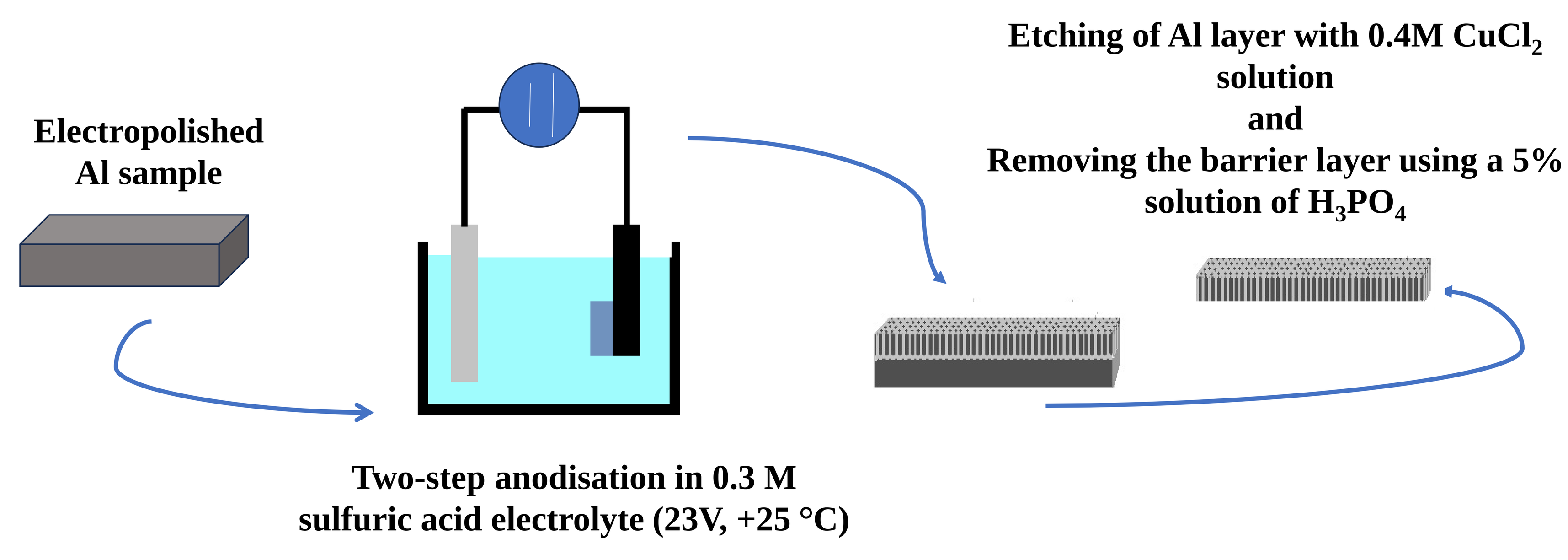


Schematic representation of the nanoconfinement effect and ion motion in single pore under applied temperature gradient

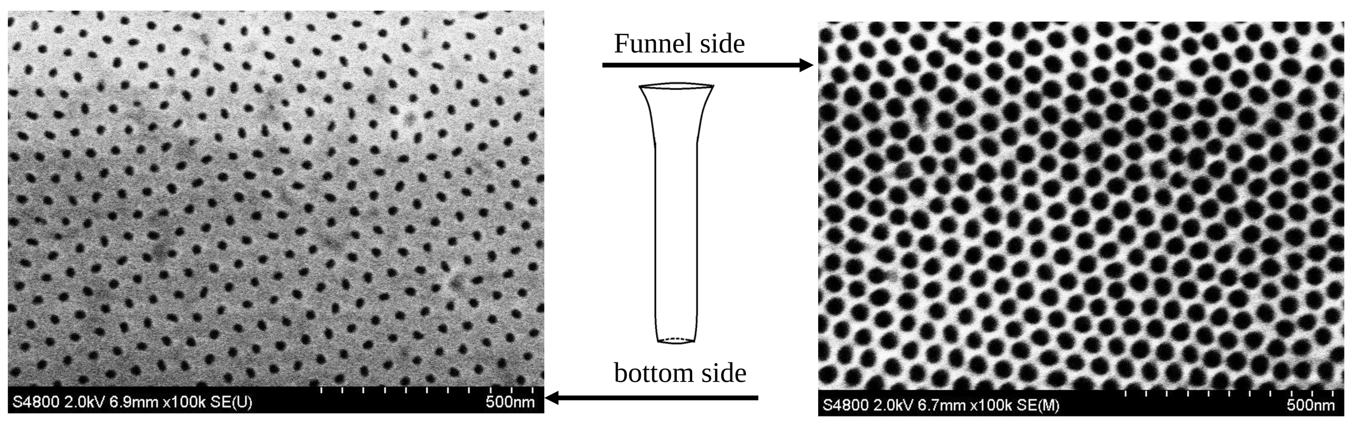
EXPERIMENTAL PART

Porous anodic alumina (AAO) is characterized by self-assembled straight cylindrical nanopores produced by electrochemical oxidation, making it particularly attractive as a material for nanofluidic platforms. The diameter and length of nanochannels can be varied by choosing optimal synthesis parameters.

High-purity (99.999%) aluminum sheet (GoodFellow) with a thickness of 0.5 mm, cut in 10×10 mm² pieces, was used for sample fabrication. Porous anodic aluminium oxide membranes have been obtained according to the standard scheme of two-stage anodization of aluminium with subsequent removal of the barrier layer.



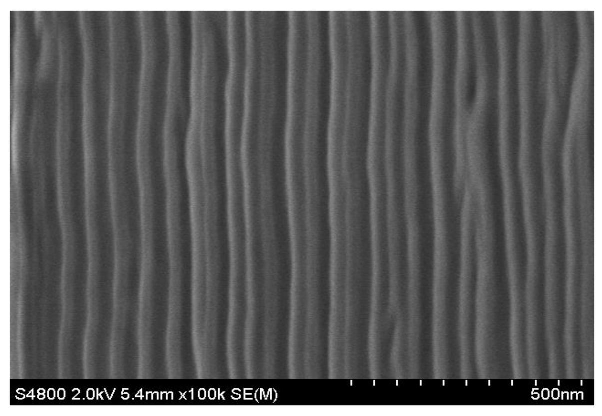
THE SURFACE ANALYSIS OF THE POROUS ANODE WAS DONE USING A SCANNING ELECTRON MICROSCOPE (SEM, Hitachi 4800).



Values of the main characteristic parameters of AAO membranes

AAO layer thickness, µm	Pore diameter, nm	Porosity, %	Pore density, number/cm²	Pore volume, nm³
50±1	23±3	14.3±0.7	28.5·10⁹	2.4·10⁷

AAO membrane cross-section

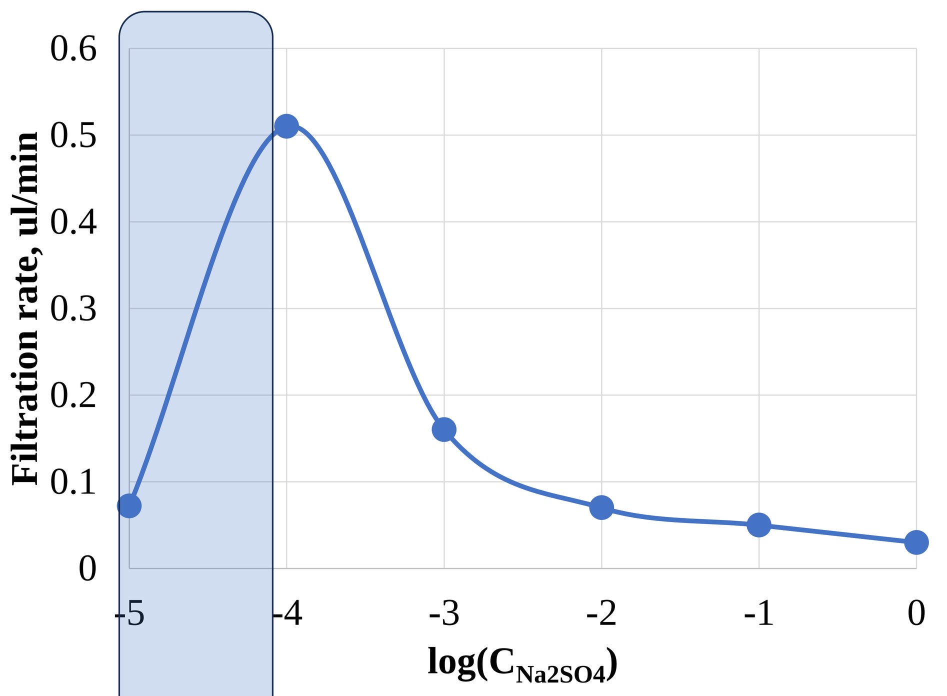


RESULTS AND DISCUSION

One of **the main challenges** in the effective application of AAO membranes in different nanodevices is **control of the nanopore filling and percentage of the active nanopore channels**, which is especially important for applications involving liquid media.

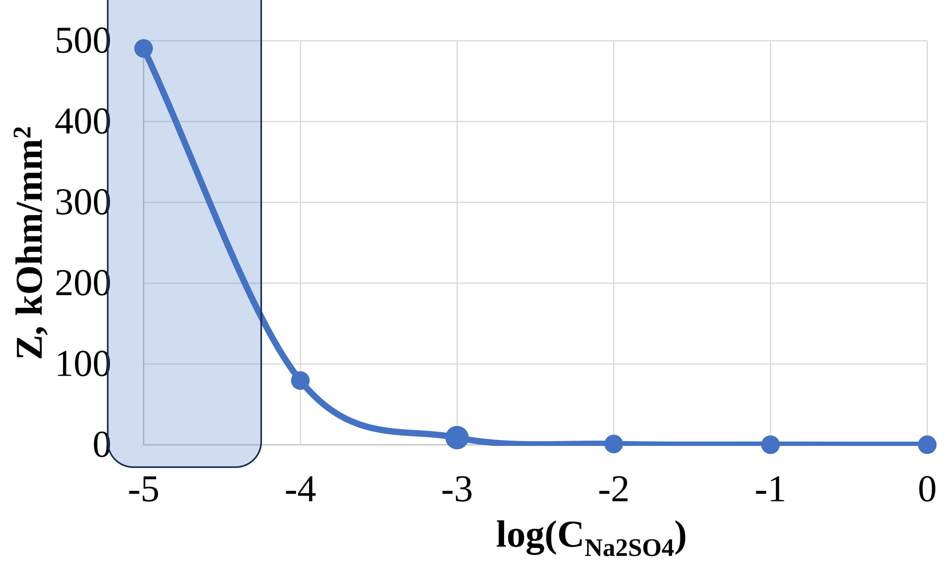
PRESSURE-INDUCED INFILTRATION OF AAO NANOCHANNELS WITH AQUEOUS Na_2SO_4 ELECTROLYTE SOLUTION

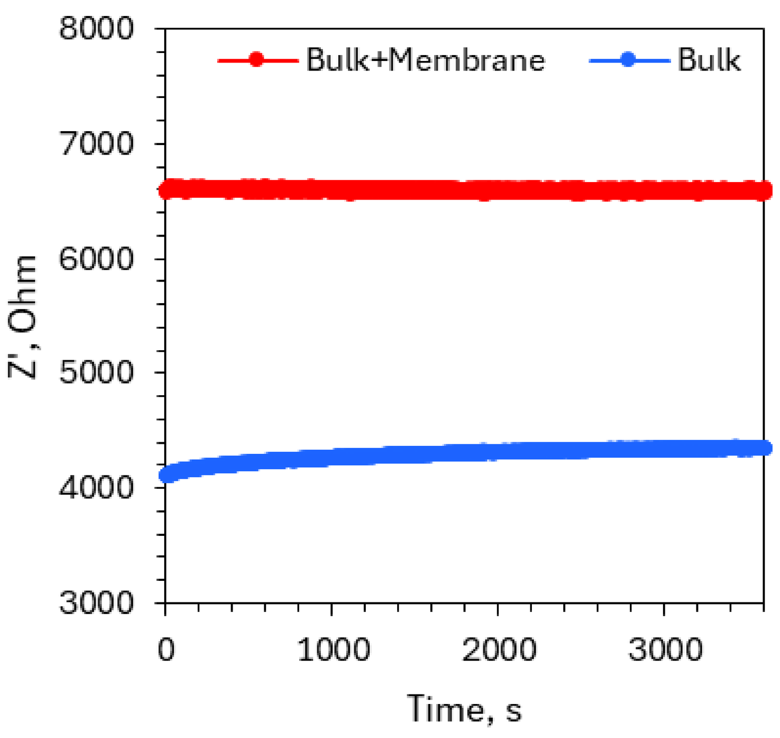
50 µm thick AAO membranes with 25 nm pore diameters have been infiltrated with aqueous Na_2SO_4 electrolyte using a ***pressure-induced infiltration*** method.
To verify electrolyte infiltration, the ionic conductance of the infiltrated AAO membranes was investigated by the means of electrochemical impedance spectroscopy (EIS).



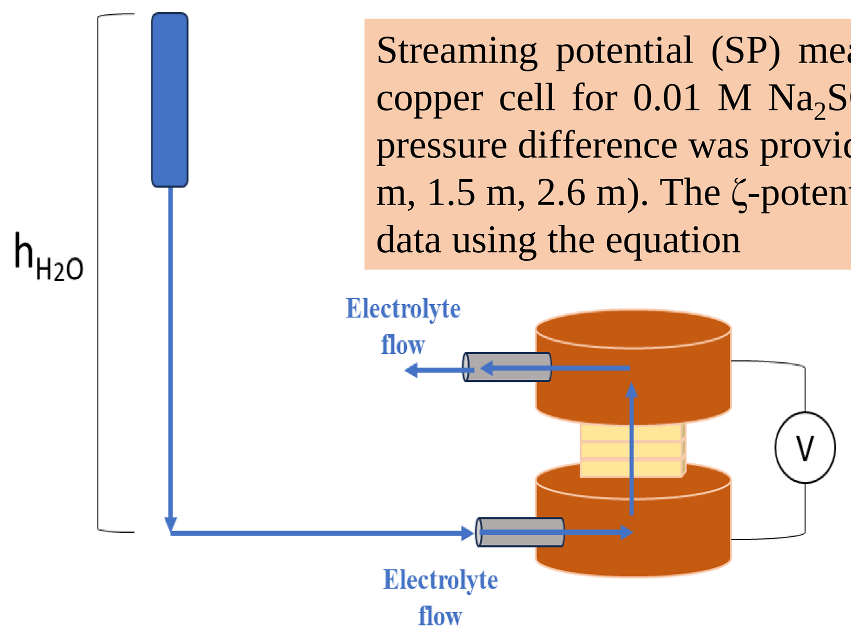
Pore channel diameter 25 nm		
C $_{Na2SO4}$, M	Filtration rate, µl/min	Z, kOhm/mm²
1×10⁻⁵	0.072	490.45
1×10⁻⁴	0.51	79.62
1×10⁻³	0.16	8.90
1×10⁻²	0.07	1.07
1×10⁻¹	0.05	0.22
1	0.03	0.09

Aluminium oxide tends to degrade in deionized water and very diluted solutions due to partial dissolution and formation of differently charged aluminum hydroxo complexes





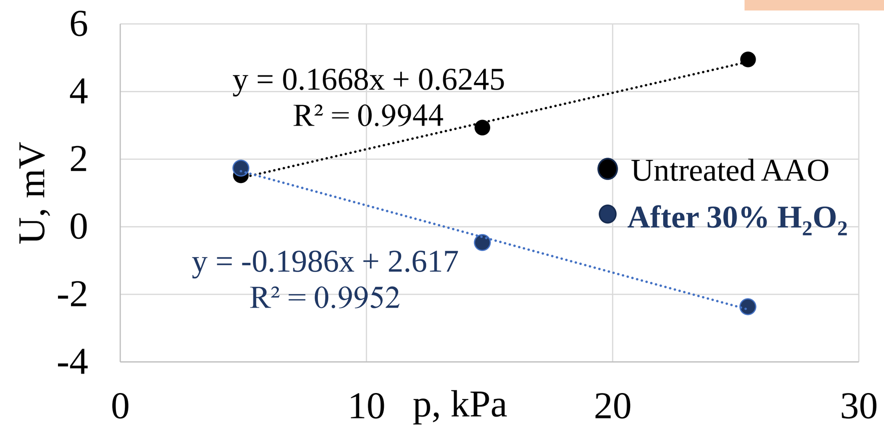
STREAMING POTENTIAL MEASUREMENTS



Streaming potential (SP) measurements were performed at room temperature in copper cell for 0.01 M Na_2SO_4 solution infiltrated into AAO nanochannels. The pressure difference was provided by different heights of the electrolyte column (0.5 m, 1.5 m, 2.6 m). The ζ-potential values were recalculated from streaming potential data using the equation

$$\zeta = \frac{dU}{dP} \cdot \frac{k\eta}{\varepsilon_0 \cdot \varepsilon_r}$$

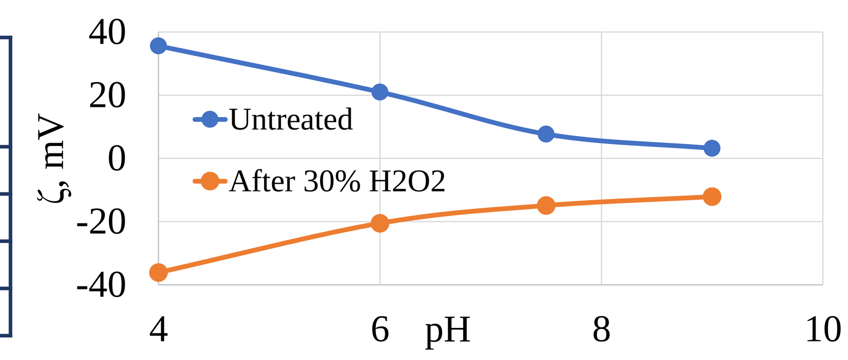
To increase the charge of the inner surface of AAO nanochannels and, as a result, to provide more efficient separation of ions, the AAO membranes were treated with a 30% peroxide solution



p, kPa	U_{str}, mV	
	Untreated AAO	After treatment with 30% H_2O_2
4.9	+1.52	+1.73
14.7	+2.93	-2.05
25.5	+4.95	-2.37

Dependence of ζ-potential on pH value

pH	Untreated AAO membrane	After treatment with 30% H_2O_2
4	+35.6	-36.1
6	+21.0	-20.5
7.5	+7.7	-14.9
9	+3.2	-12.1



CONCLUSION

- ✓ The pressure-assisted infiltration was determined to be the most efficient pore filling method, which resulted in a stable proportion of > 90 % of pores filled with the electrolyte and was used in streaming potential measurements as well.
- ✓ The impact of different electrokinetic effects, such as streaming potential, electroviscous and electroosmotic flow (EOF) effects, on value of impedance and flow rate, is especially noticeable in the case when EDL are completely or partially overlapped, which may occur in *25-nm-pore*-AAO nanochannels when using a very diluted solution (C(Na_2SO_4) >10⁻³ M).
- ✓ However, at a concentration of 1·10⁻⁵ M, membrane degradation occurs due to partial dissolution and formation of differently charged aluminum hydroxocomplexes.
- ✓ Efficiency of energy conversion in nanoconfined electrolyte-based systems can be increased by modifying the nanochannel inner surface charge. Treatment of AAO membrane with 30% peroxide solution changed the ζ potential from positive to negative value.

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