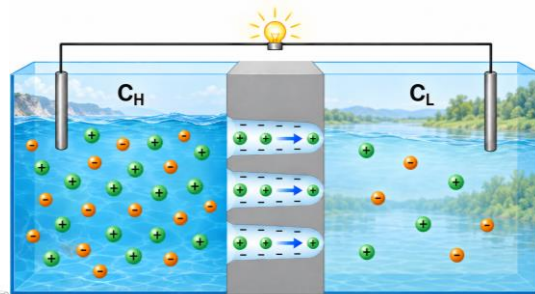


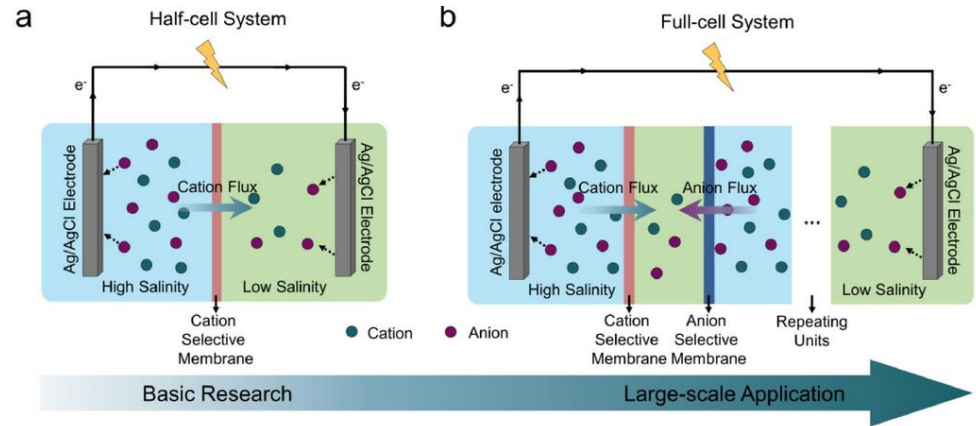
Insights into Scaling of Osmotic Power in Bullet-Shaped Nanochannels



Dila Kaya, Onur Cem Polat, Gregorio Laucirica,
Maria Eugenia Toimil-Molares

Power from Salinity Gradients

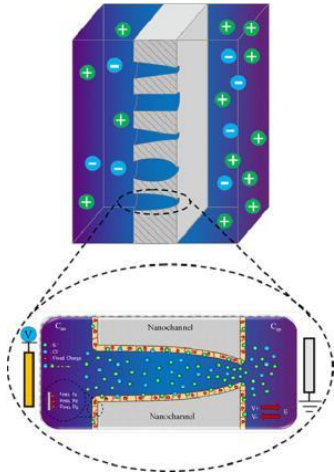
- Salinity gradient energy is a largely **untapped energy resource**
- Nanofluidic reverse electrodialysis: **ion-selective nanochannels** convert a salt concentration gradient into electrical current
- **Track-etched polymer membranes** offer **tunable channel geometry and density** to investigate their impact on maximum power output



Chen, W., Xiang, Y., Kong, X. Y., & Wen, L. (2022). *Giant*, 10, 100094.

Scalability of Osmotic Energy Harvesting

Single Nanochannels



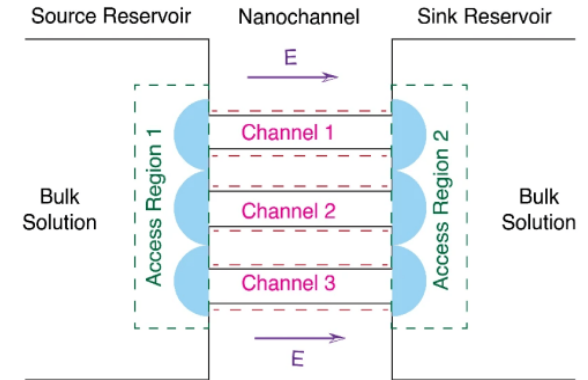
Single bullet nanochannels demonstrate **superior power output***

Addressing the Gap

Energy-conversion performance across **low channel densities**

Where does linear scaling actually break down?

Multi-Pore Membranes



Overlapping access regions and **concentration polarization** reduce contribution of each channel

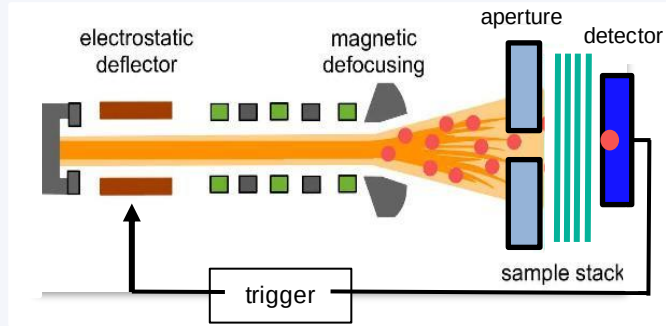
*Laucirica, G., et al. (2020). *Nano Energy*, 71, 104612.

Siwy, Z. S., et al. (2023). *Chem.Soc. Rev.*, 52(6), 1983.

Manikandan, D., et al. (2024). *2D Mat. and App.*, 8(1), 47.

Fabrication of Bullet-Shaped Nanochannels

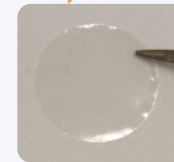
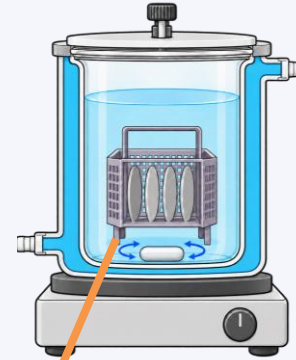
1. Ion-track formation



2. One-sided UV exposure for 24 hours:

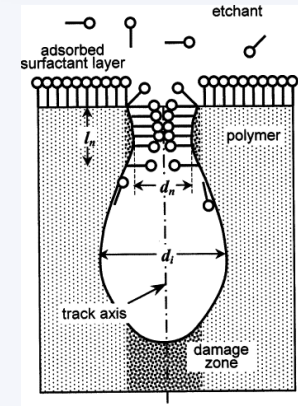
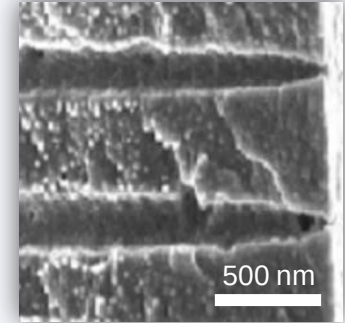
- Increases susceptibility to chemical attack.
- Decreases hydrophobic binding to surfactant.

3. Chemical etching



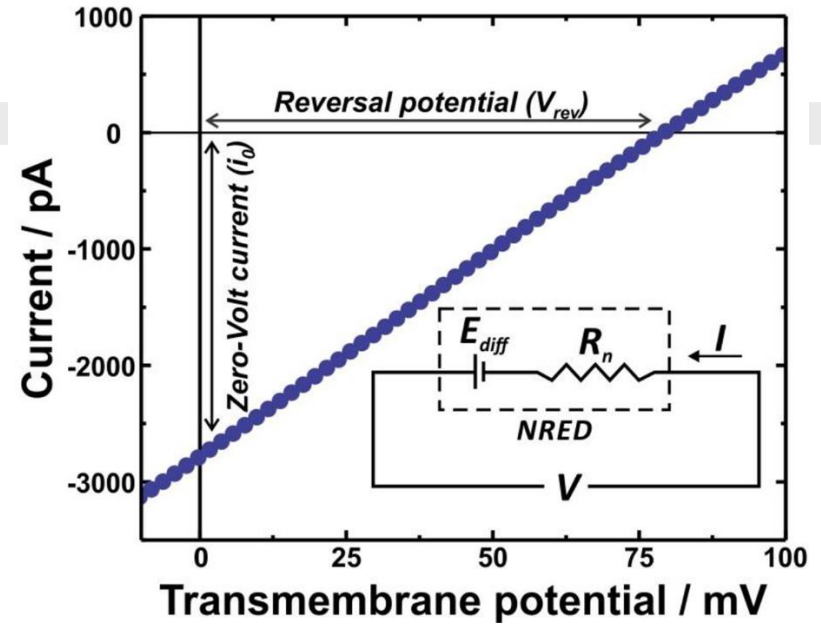
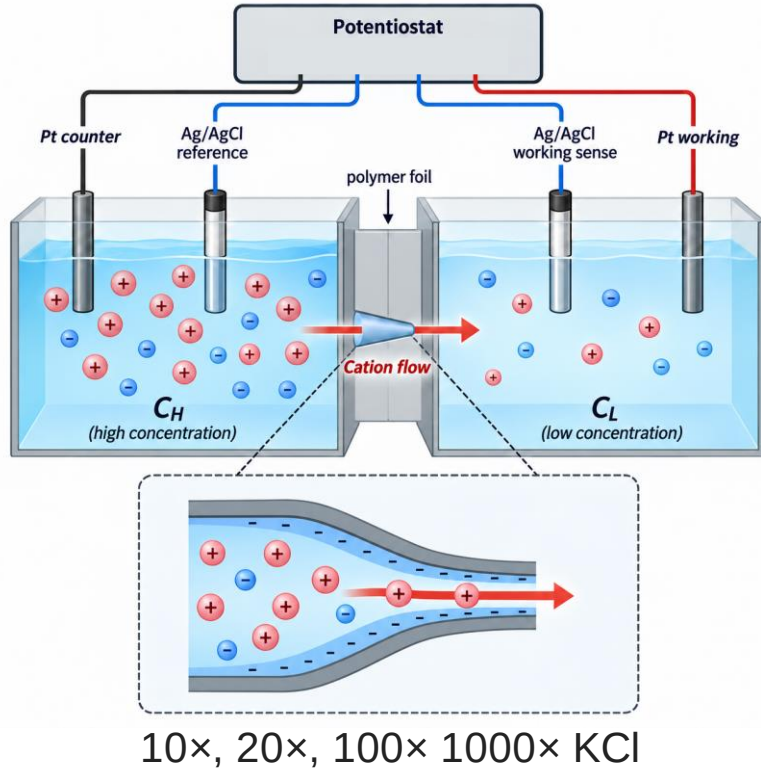
12 μ m
PET
Membrane

6 M
NaOH
surfactant,
60°C,
4 -10 min



Apel, P. Y., et al. (2007), *Nanotechnology*, 18(30), 305302.

Energy Conversion Measurements

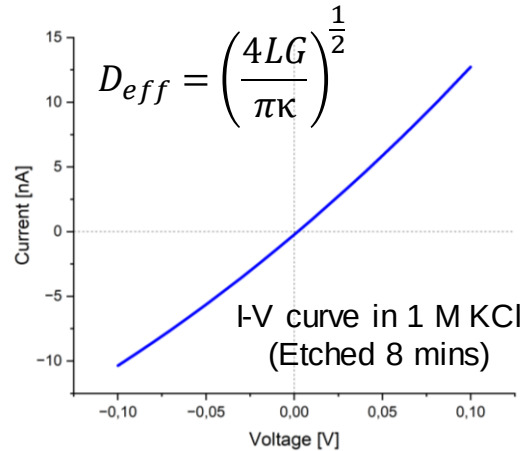


$$P_{max} = \frac{i_0 V_{rev}}{4}$$

Laucirica, G., et al. (2020). *Nano Energy*, 71, 104612.

Electrochemical Characterization

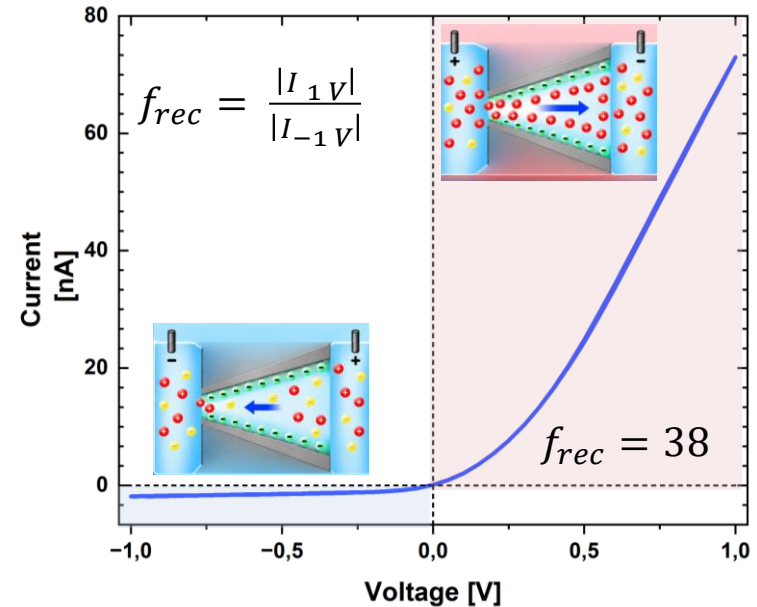
Effective Diameter



Etching time (mins)	4	6	8	10
D_{eff} (nm)	205	320	410	520

$$D_{eff} = (51.3 \text{ nm min}^{-1}) t + 2.5 \text{ nm}$$

Rectification

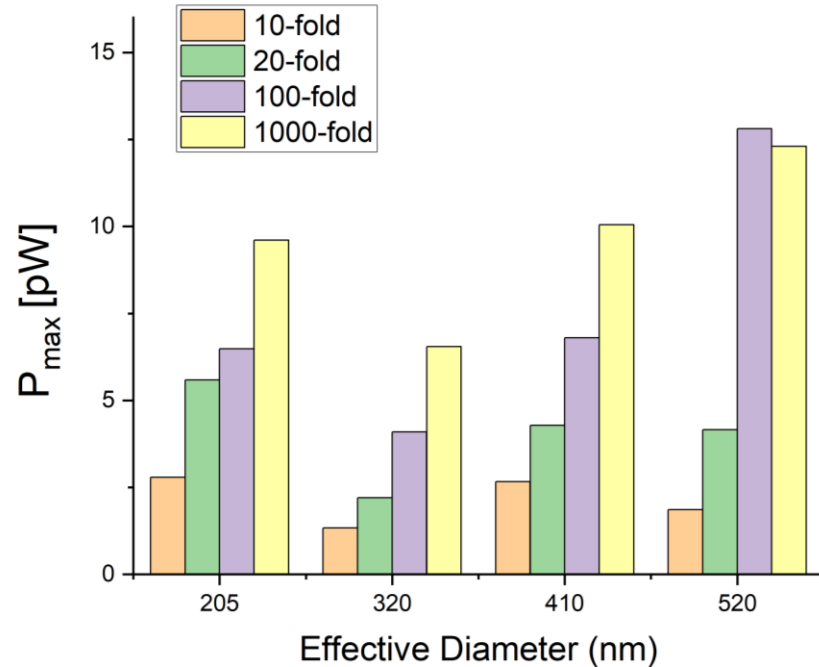


I-V curve in 0.1 M KCl ($D_{eff} = 410 \text{ nm}$)

Single Nanochannel Power Output

Highest $P_{\max}$:

- **1000x concentration gradient**
- 10 min etched sample / 520 nm

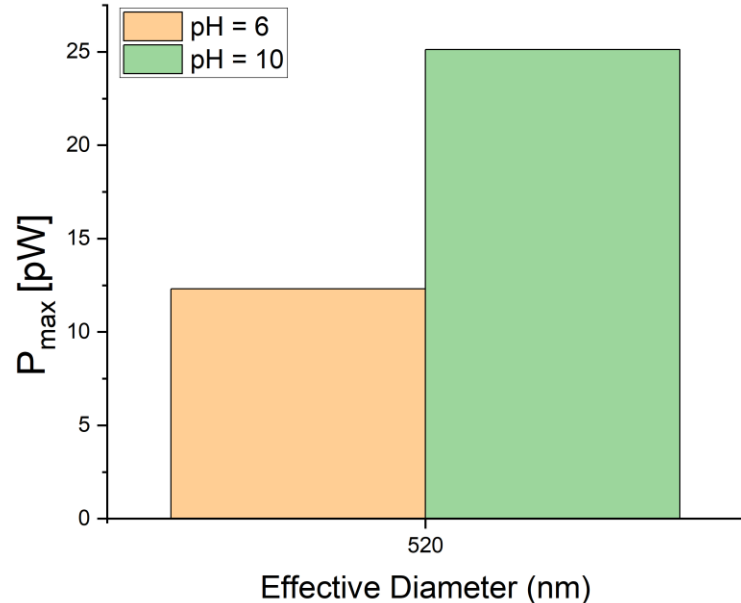


Single Nanochannel Power Output

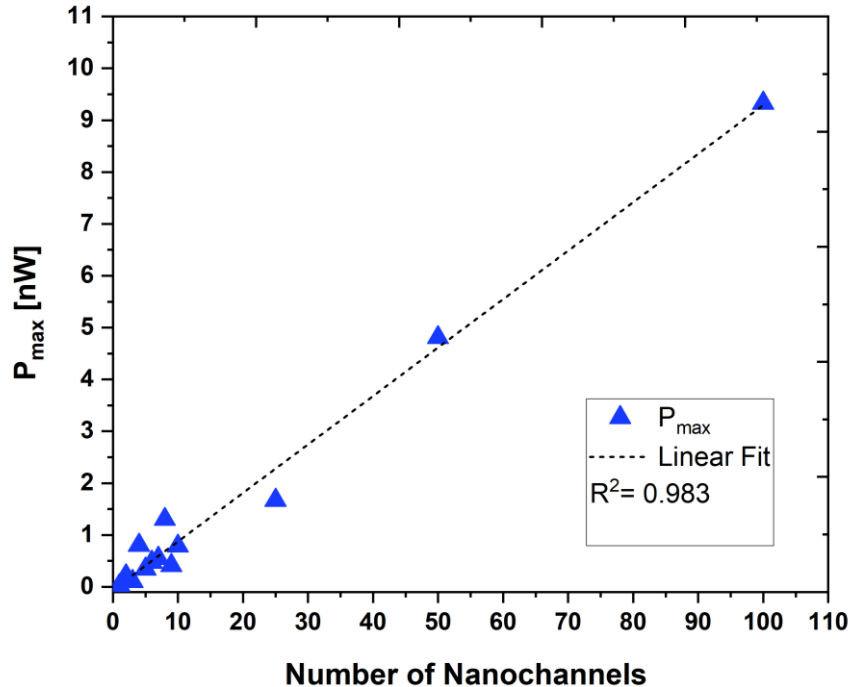
Highest $P_{\max}$:

- **1000x concentration gradient**
- 10 min etched sample / 520 nm
- At **pH = 10**
 $P_{\max}$ increases from 12 to 25 pW

Higher pH $\rightarrow$ promotes deprotonation
on nanochannel wall $\rightarrow$ stronger cation
selectivity



1 – 100 Nanochannels

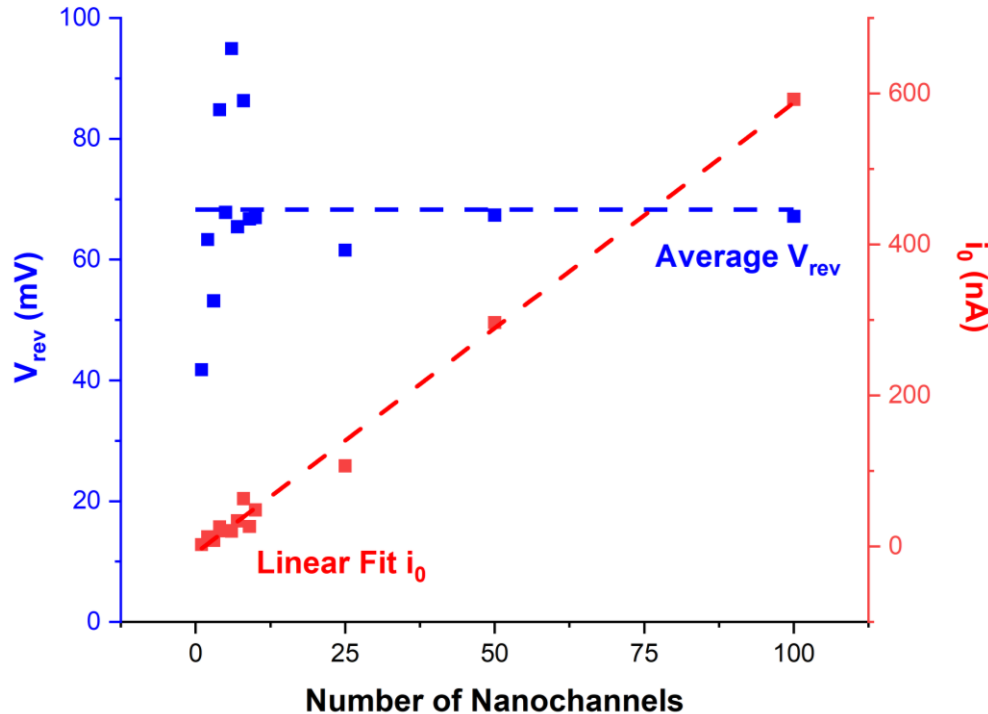


Maximum power output scales
linearly up to 100 nanochannels

Average $P_{\max}$ per nanochannel is
~87 pW, in agreement with ~80 pW
previously reported by Laucirica et al.

Laucirica, G., et al. (2020). *Nano Energy*, 71, 104612.

1 – 100 Nanochannels



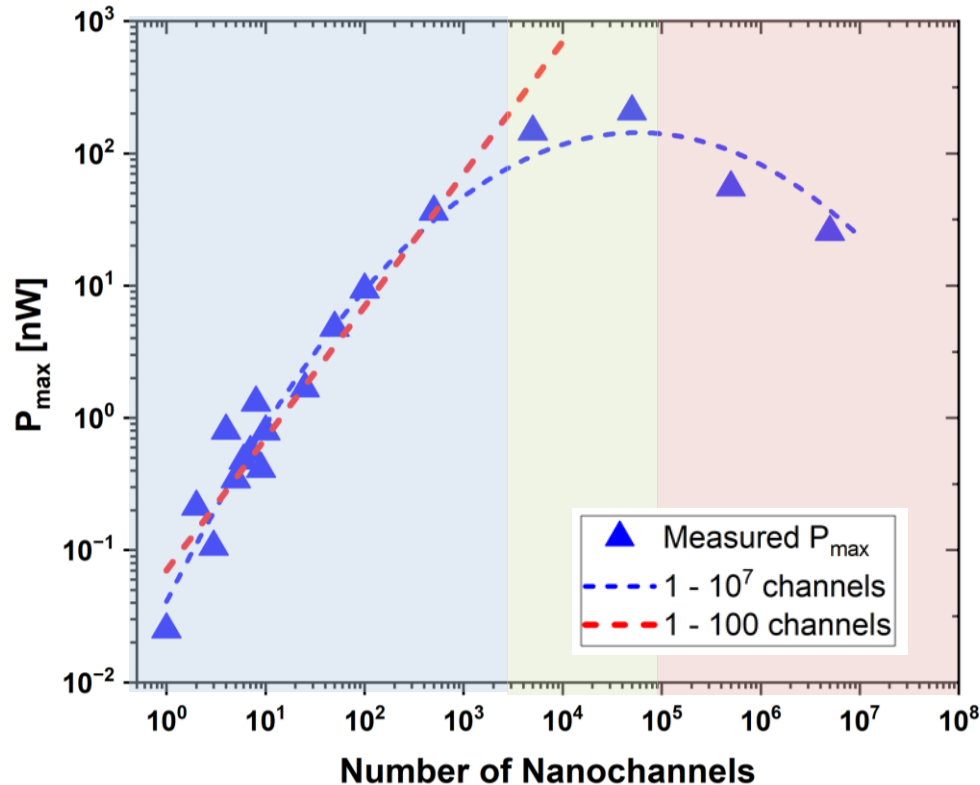
At low density and identical salt concentration gradient (1000-fold), additional nanochannels **linearly increase current without reducing reversal potential**

$$V_{rev} = 68 \pm 13 \text{ mV}$$

$$i_0 = (6.0 \pm 0.15) \text{ nA} - 8.8 \text{ nA}$$

$$R^2 = 0,992$$

Extending to Higher Fluences

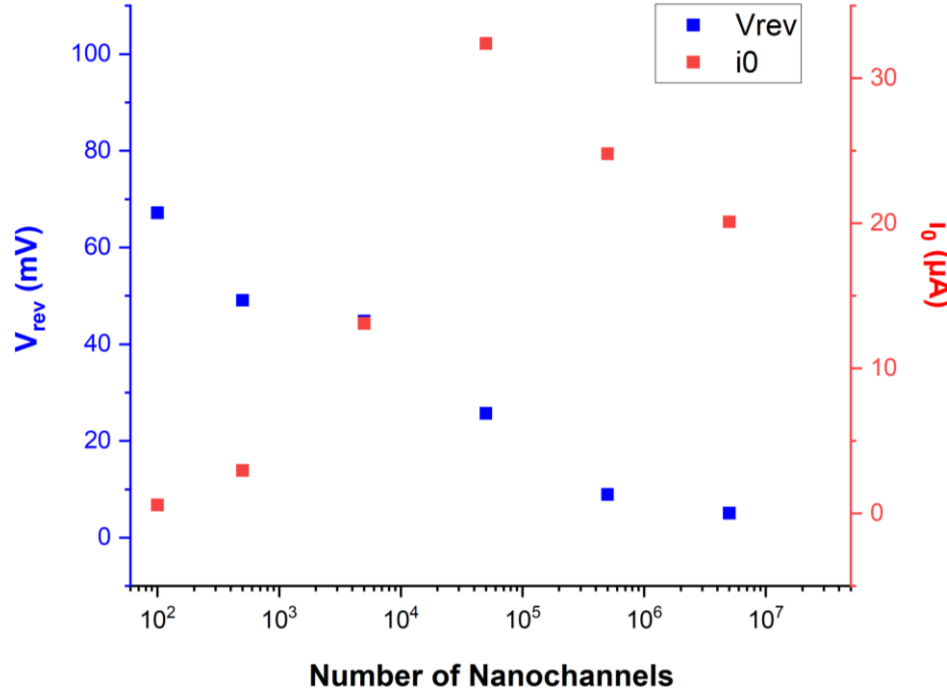


Channels act largely independently

Depletion/ enrichment zones of neighboring channels begin to overlap

Interpore interactions start to dominate

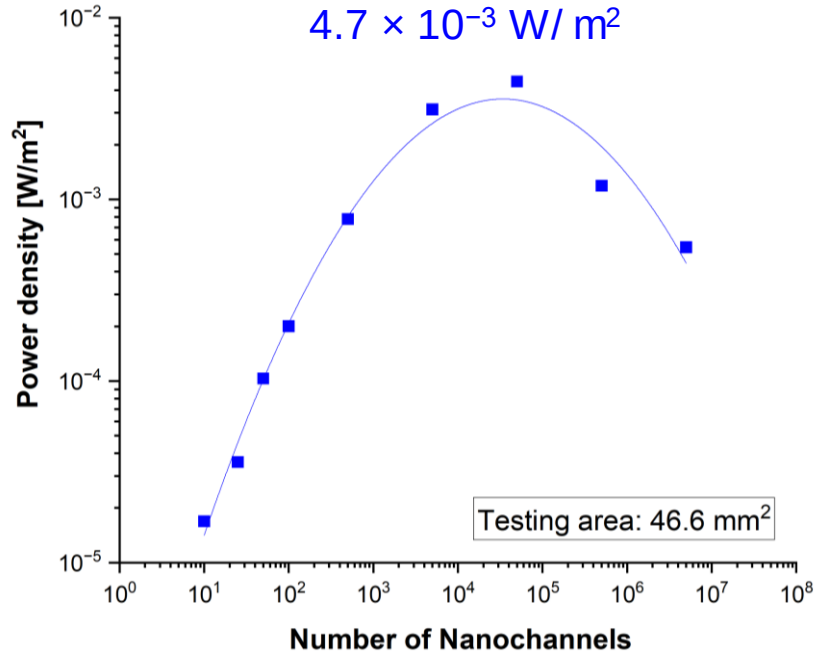
Extending to Higher Fluences



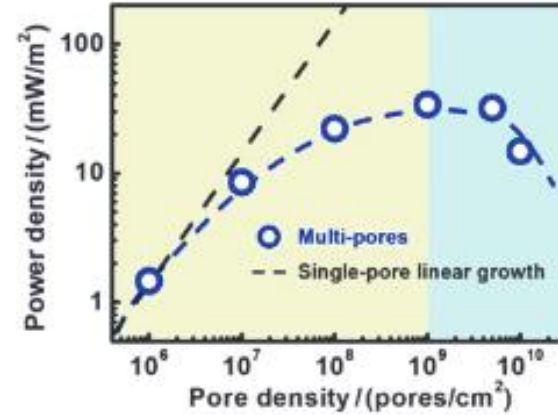
At high density, V_{rev} decreases and i_0 no longer scales proportionally

This indicates **loss of charge selectivity** due to concentration polarization

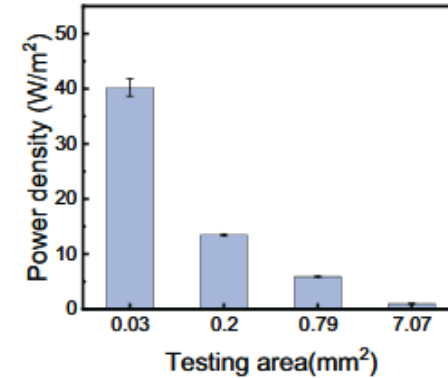
Power Density Comparison



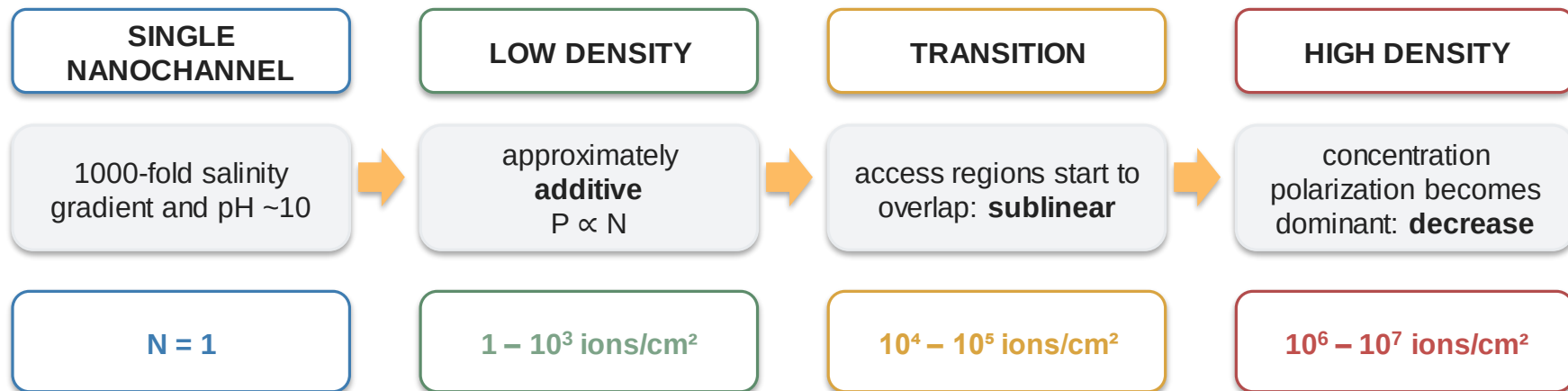
Commercial Goal: 5.0 W/ m²



Su, J., et al. (2018). *Chinese Journal of Chemistry*, 36(5), 417-420.



Duan, R., et al. (2024). *Adv. Func. Mat.*, 34(12), 2311258.



Next Steps

- Surface/ geometry optimization
- Coupled effects with thermal gradient
- Membrane thickness and test area optimization

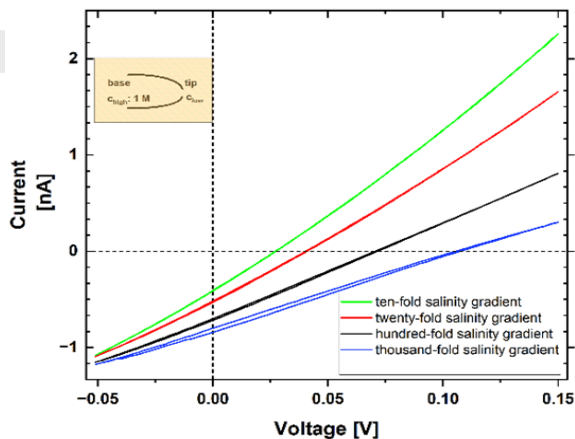
Dialogue between single and multipore research can be established via low/ intermediate nanochannel densities

THANK YOU!

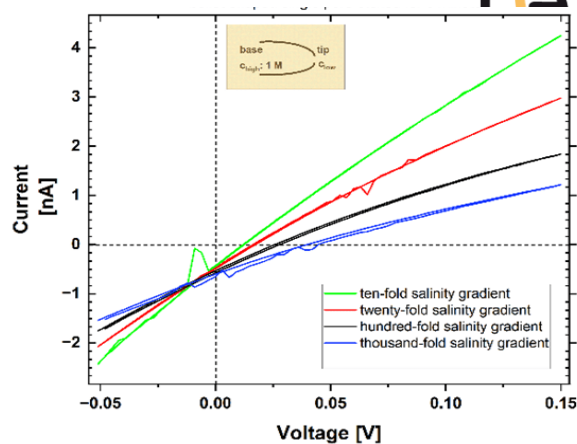


Results presented here are based on an experiment, performed at the X0 beamline of GSI Helmholtzzentrum für Schwerionenforschung, Darmstadt (Germany) in the frame of FAIR Phase-0

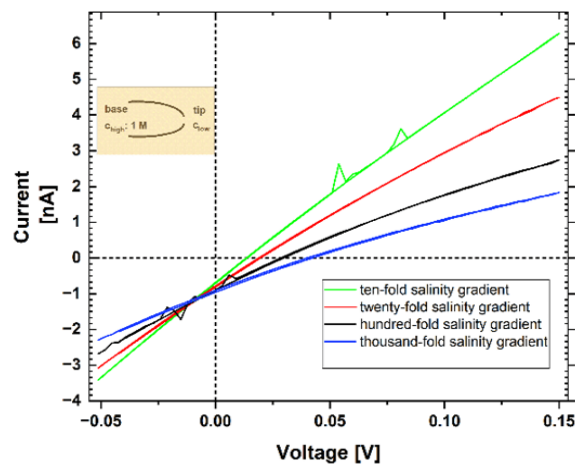
4 min.



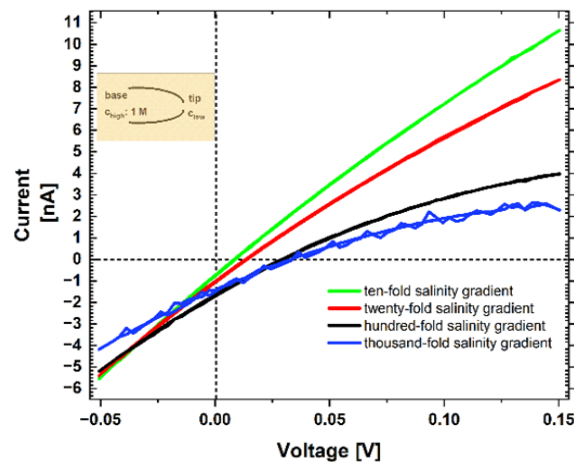
6 min.



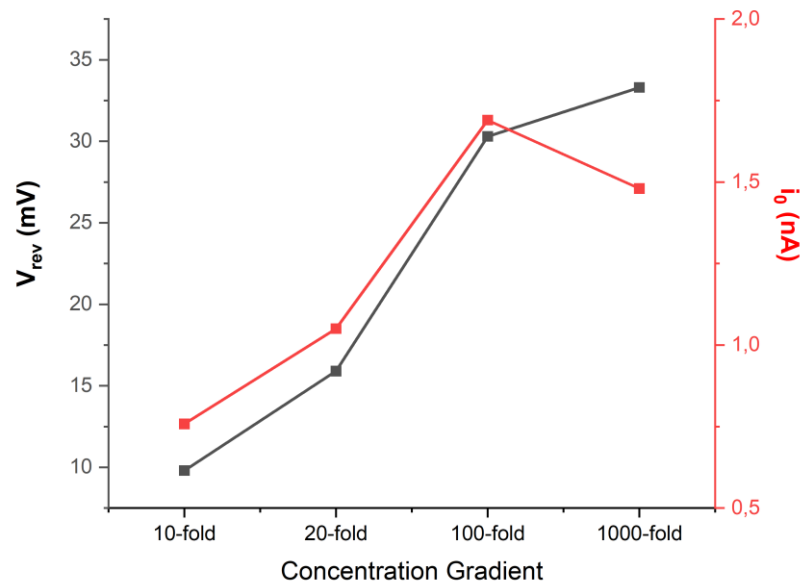
8 min.



10 min.

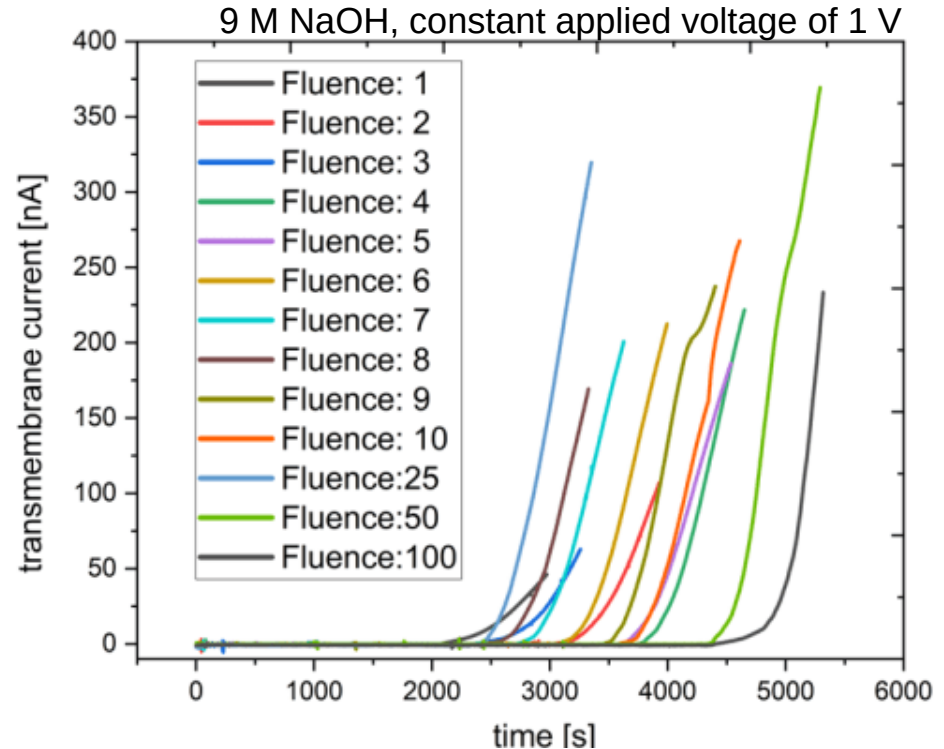


Concentration gradient on V_{rev} and i_0

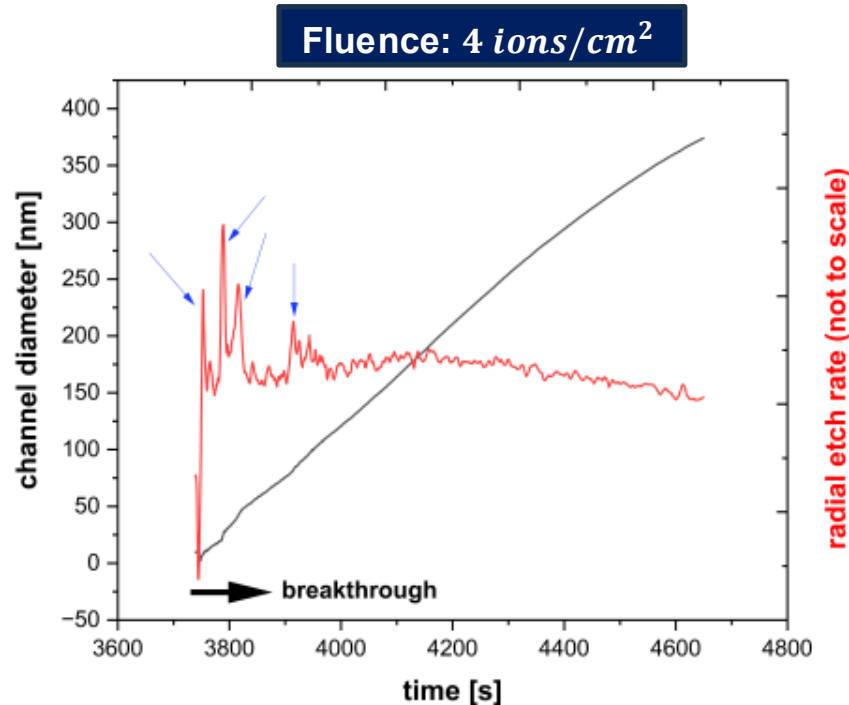


Cell-etching curves of low-fluence cylindrical PET nanochannels

- Determination of the **nanochannels available** for ion transport after etching by I-t measurements
 - Room temperature cell-etching with lower etching rate
- ➔ higher temporal resolution of the etching process
- Duration for the first breakthrough event observations independent of fluence

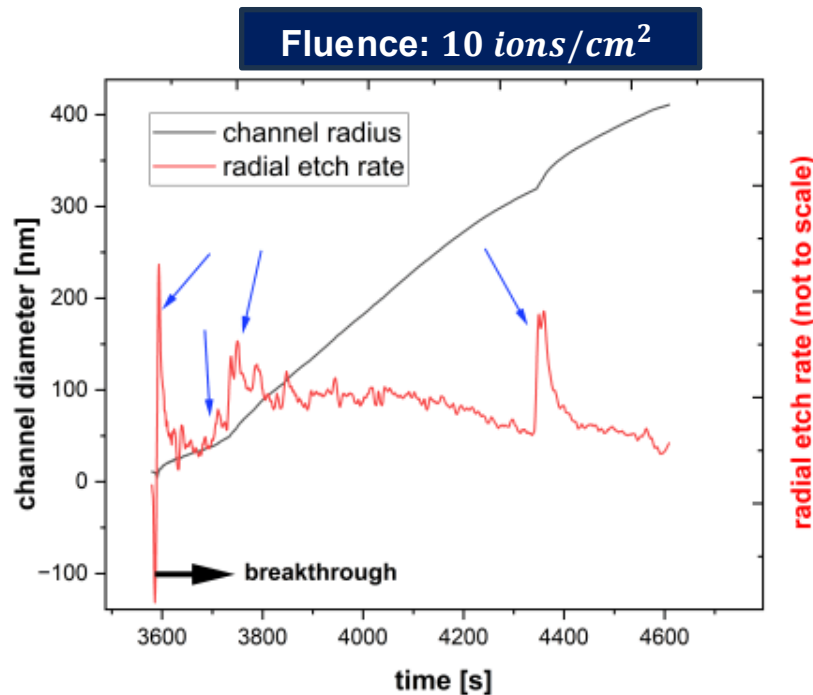


Cell-etching curves of low-fluence cylindrical PET nanochannels



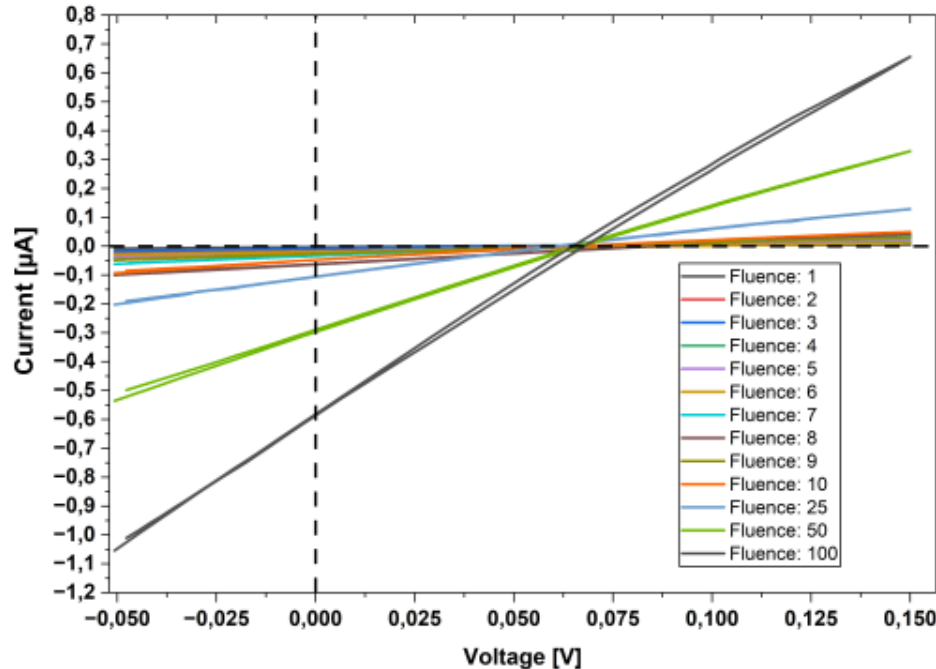
- At sufficiently large $\frac{v_t}{v_b}$ ratio, the nanochannel can be approximated as a **cylinder with an effective radius** $r_{eff} = \sqrt{\frac{L}{\pi \sigma U}}$
- **Radial etch rate** defined as:
$$v_r = \frac{\Delta r_{eff}}{\Delta t}$$
- Peaks in the graph as indicators of a new breakthrough event

Cell-etching curves of low-fluence cylindrical PET nanochannels



- Graphically distinguishing the breakthrough events as current increases at **higher fluences proved in this case to be ineffective**
- Prone for external mechanical stimuli and differentiating overlap of peaks
- Can be further improved via the usage of a Faraday cage and improved data analysis

ENERGY CONVERSION PERFORMANCE OF LOW-FLUENCE (1-100) BULLET-SHAPED NANOCHANNELS



- The reversal potential V_{rev} is observed to stay within a reasonably small interval, as the zero-voltage current i_0 scales with the increasing fluence
- Rectification performances of each membrane were separately recorded

Energy conversion performance of low-fluence ($1\text{-}10^2$ ions/cm²) bullet-shaped PET nanochannels



Nominal fluence [$P_{\max \text{ per pore}}$]	$P_{\max}$ [pW]	$P_{\max \text{ per pore}}$ [pW]
1	25	25
2	212	106
3	106	35
4	802	200
5	343	69
6	474	79
7	551	79
8	1301	163
9	411	46
10	787	79
25	1668	67
50	4807	96
100	9329	93

- Higher $P_{\max \text{ per pore}}$ values for certain membranes may suggest synergical interactions between pores
- Highest single-pore $P_{\max}$ value for bare track-etched bullet-shaped nanochannels reported by Lauricia et al. ~ 80 pW.
- Analysis of the spatial distribution and number of nanochannels on the membrane surface can aid investigating coupling effects