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Design and characterization of highly charged interfaces

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Introduction

Blue energy is a low carbon, non-intermittent energy source (Fig. 1). Up to now the existing methods for its harvesting fail to deliver enough electrical power, which makes them unsuitable for commercial realization. Nevertheless, in 2013 A. Siria *et al.* proposed a new mechanism, which can significantly boost the process's efficiency[1]. Their idea is to employ novel membranes that use the so-called diffusio-osmosis electrokinetic phenomenon (Fig. 2). A key factor for their good performance is the large surface charge of their pores through which the solution passes. The primary goal of our project is to enhance this parameter, thus making possible the facile production of low-cost membranes. We study the possibility of preparation of highly charged glass surfaces *via* adsorption of polyoxometalate (POM) ions. To perform the investigation, we needed a proper probing tool, so we built a simple device for fast measurement of surface charge, based on zeta potential evaluation.

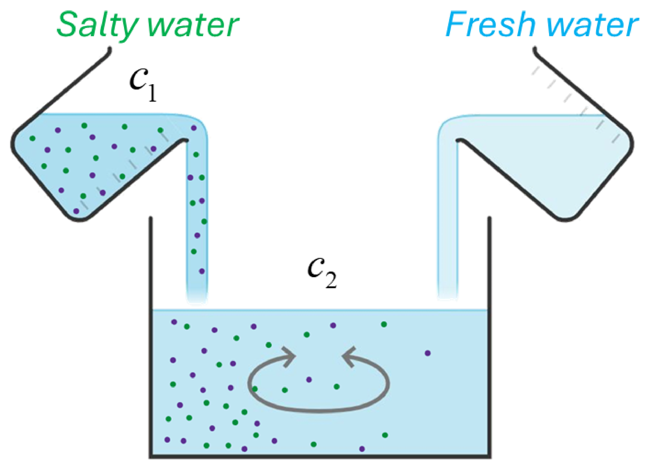


Fig. 1: Mixing of solutions with different salinities, the source of *blue energy.*
Free energy released:
$\Delta_{\text{mix}}G \approx n_{solute}RT\ln(C_2/C_1) < 0$

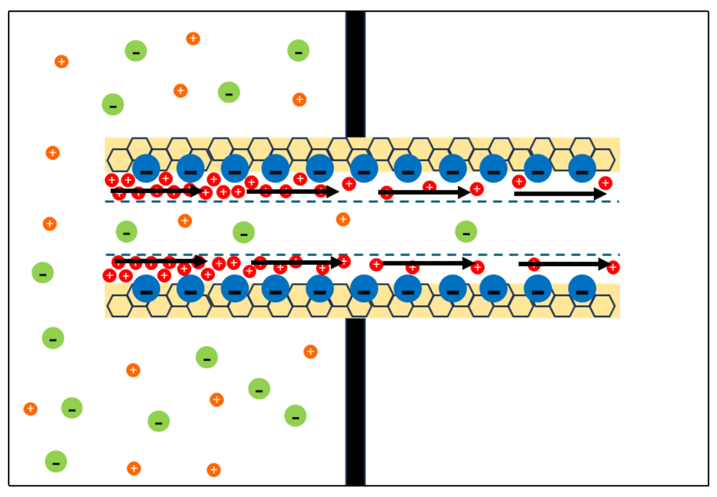


Fig. 2: Diffusio – osmosis, the novel mechanism for blue energy extraction proposed by A. Siria *et al.*

Achieving large surface charge

1. Strategy

- Adsorption of Al_{13}^{7+} ε-Keggin type POM (Fig. 3) on glass surfaces;
- Highly-charged units with affinity towards glass surfaces.

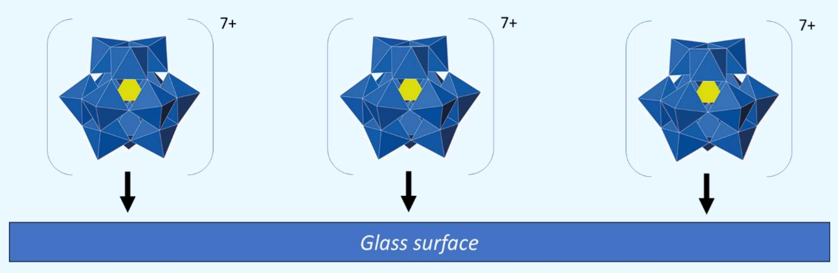


Fig. 3: POM with formula $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ adsorbed on glass surface.

2. Synthesis and characterization

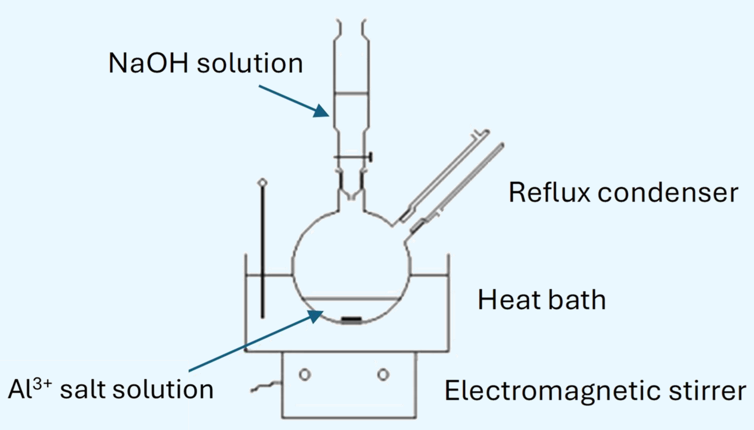


Fig. 4: Synthetic procedure for obtaining Al_{13}^{7+} POM.

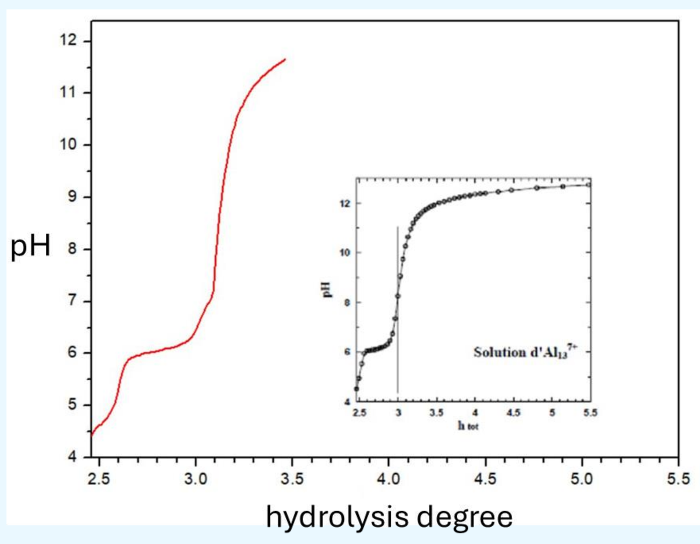


Fig. 5: Potentiometric titration of obtained solution.

3. Adsorption on glass and surface characterization

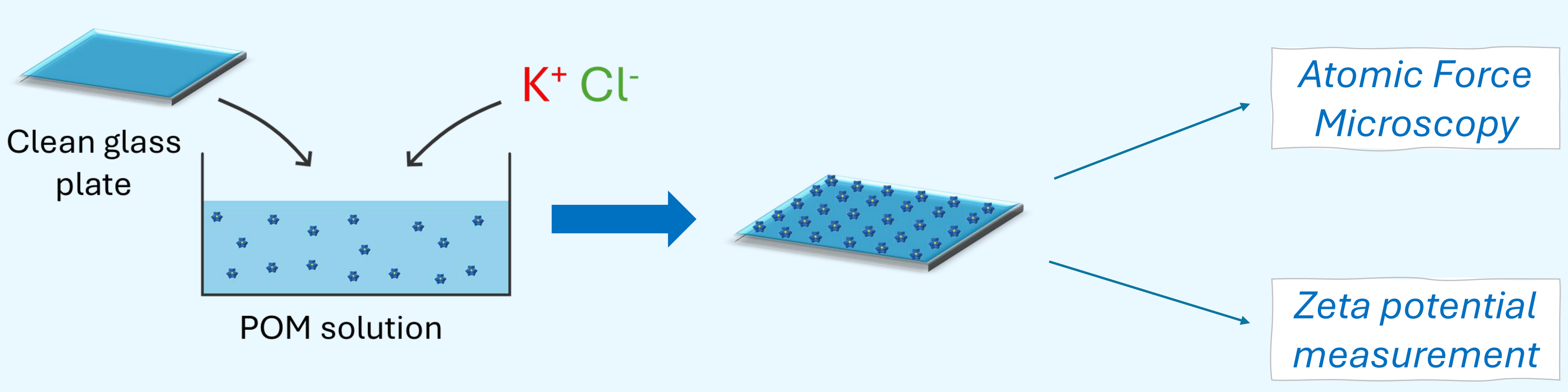


Fig. 6: POM adsorption and surface characterization methods.

Measurement of surface charge

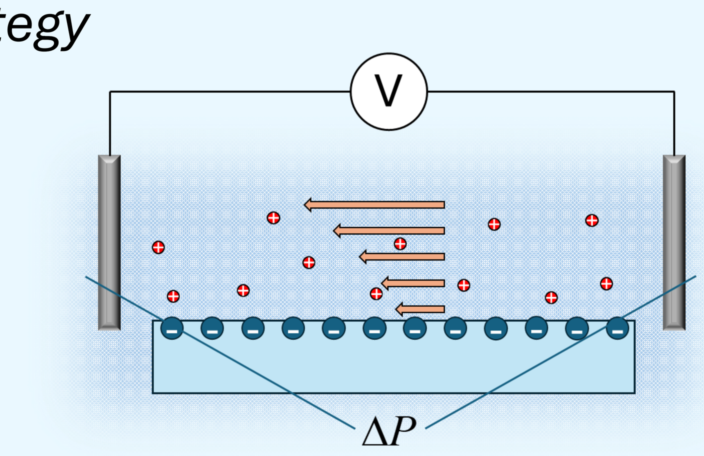
1. Strategy

- Zeta potential ζ measurements:

$$q = \sqrt{8C_0\varepsilon RT}\,\sinh\left(\frac{F\zeta}{2RT}\right)$$

q – Surface charge density in C m^{-2}

- Inducing electrokinetic phenomena:
  - Electroosmotic flow
  - Streaming current
  - Streaming potential



$$\Delta V_{s.p.} = (\varepsilon/\eta\sigma)\zeta\,\Delta P$$

Fig. 7: Streaming potential.

2. The device

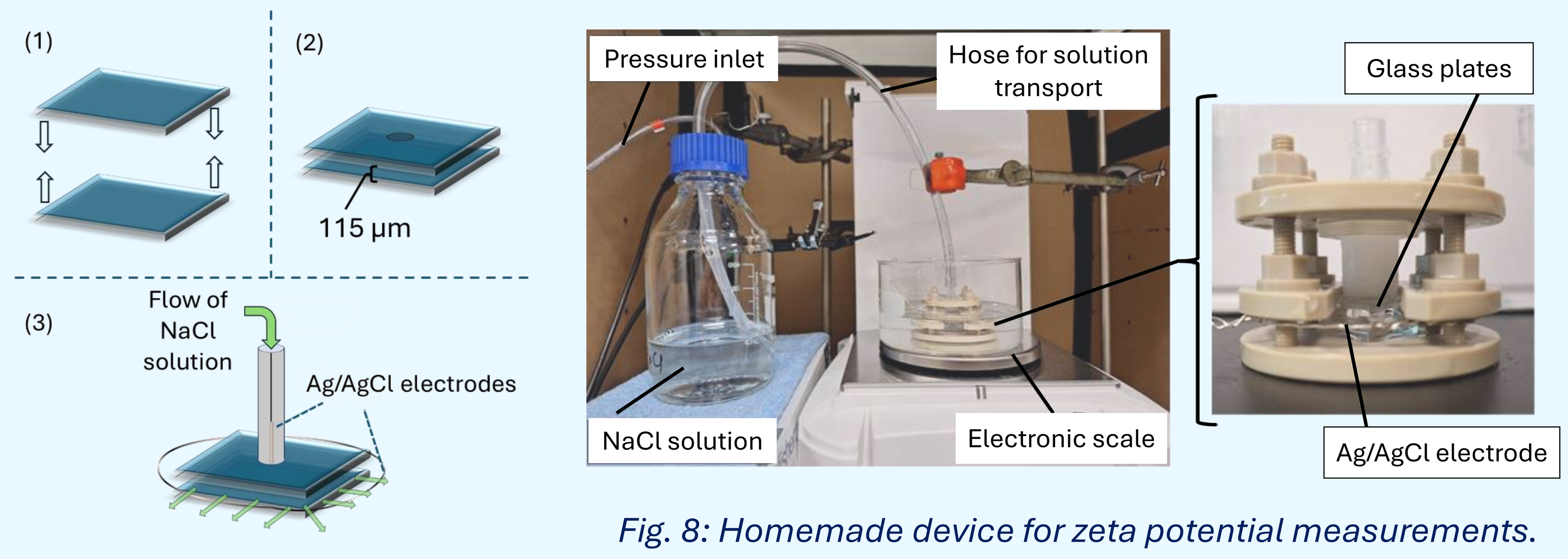


Fig. 8: Homemade device for zeta potential measurements.

3. Results from bare glass measurement

pH	Zeta potential, mV	Surface charge density, mC/m^2
neutral	-88	-10
2.8	-50	-4
10	-146	-32

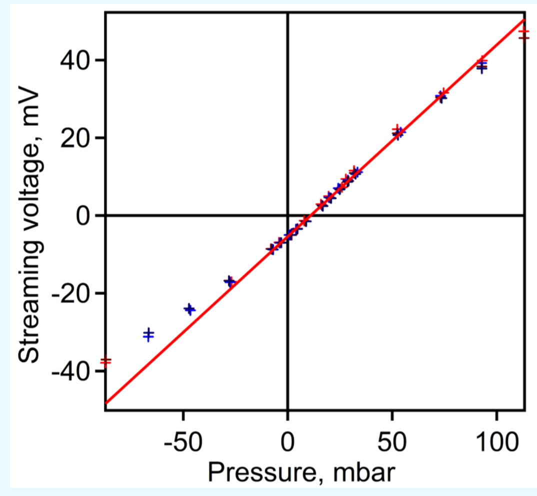


Fig. 9: Streaming potential at neutral pH.

Results from glass with adsorbed POM

- Streaming potential at neutral pH
- Result: $\zeta = +67\ mV$
  $q = +6.4\ mC/m^2$
- Induced difference in surface charge:
  $\Delta q = 16.4\ mC/m^2$

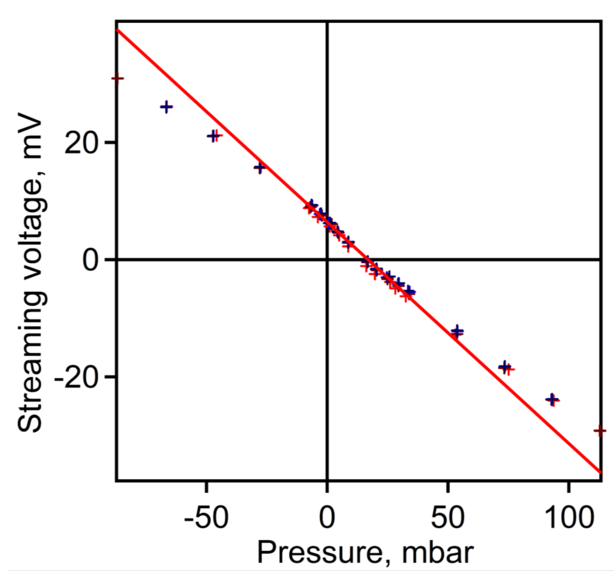


Fig. 10: Streaming potential of POM-covered glass at neutral pH.

Conclusion

We have successfully developed a method for inducing surface charge by adsorption of Al_{13}^{7+} ε-Keggin type POM. Together with this, we have built a simple device for zeta potential measurement, which allows us to probe the surface charge of the POM-treated glasses. Future efforts will be dedicated to the optimization of the POM deposition conditions (temperature, immersion time, KCl amount) in order to achieve extremely large surface charges.

References:

1. Siria, A., Poncharal, P., Biance, A.-L., Fulcrand, R., Blase, X., Purcell, S. T., & Bocquet, L. (2013). Giant osmotic energy conversion measured in a single transmembrane boron nitride nanotube, Nature, 494(7438), 455–458