

Inducing Monovalent-Selectivity in Cation Exchange Membranes using Atomic Layer Deposition

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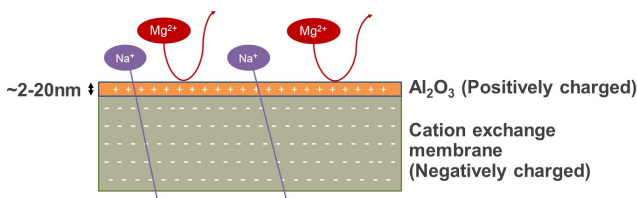
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Summary

We used the **Atomic Layer Deposition** technique to deposit thin layers of **positively-charged Al_2O_3** on negatively charged **cation exchange membranes**, aiming to enable **selectivity between cations with different valency**, such as Na^+ and Mg^{2+} . Such selectivity can enable **healthier desalination** and a variety of other processes.

Why ALD?

- Extremely **precise control** over thin layer thickness
- Ability to deposit various compounds, including **high-IEP metal oxides** that can have **high charge densities**
- Applicable to most substrates
- Homogenous & conformal cover



Why Al_2O_3 ?

- Positive charge** in aqueous solutions of relevant pH conditions
- Well established ALD process** including in low temperatures
- A stable compound** in aqueous solutions of relevant pH conditions

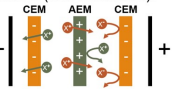
Our results show that while **we manage to deposit a positively-charged layer in the required low temperatures** for the thermally-sensitive polymer, the layer is **unstable in solution**. We link this instability to weak bonding between the layer and the membrane surface and suggest plans to overcome this obstacle.

Motivation

- Desalination processes remove ions without discrimination, including ones vital for our health, such as Mg^{2+}
 - Lack of Mg^{2+}** in desalinated drinking water is estimated to be responsible for **hundreds of deaths** each year in Israel alone².
 - Electrodialysis with monovalent selective CEMs could enable **healthier processes for brackish water desalination**.
 - High resistance and low selectivity** of commercially available monovalent-selective CEMs inhibit widespread adoption of this technology.¹
- Our goal is to use ALD technology to develop new monovalent-selective CEMs with high selectivity and low resistance.

Background

- Cation exchange membranes (CEMs)** are negatively charged polymers that only permit passage of cations (and not anions).
- Electrodialysis** desalitates water by applying a potential to move ions between parallel flow channels. (figure on the right)
- Monovalent-selective CEMs** preferentially let through monovalent cations (with +1 charge) over multivalent ones (with higher charge).
- Mechanisms for monovalent-selectivity** are typically based on:¹
 - Electrostatic repulsion** – a positively-charged layer on top of the negatively-charged CEM repels multivalent ions stronger than monovalent ones.
 - Steric hindrance** – a dense layer prevents multivalent ions from entering the membrane based on their larger hydration shells.

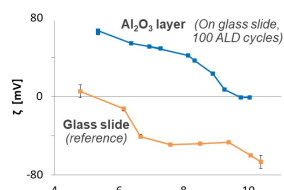


Results

Al_2O_3 ALD was performed at 40°C, on both glass slides and Cation Exchange membranes, and characterized in several aspects:

ζ potential

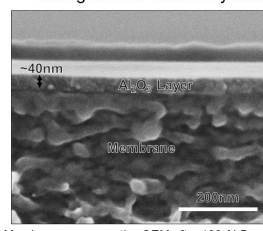
Positive surface potential in the required pH range, up to the IEP at pH of ~9.5



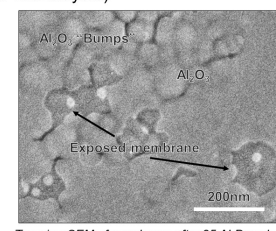
Zeta potential of the deposited layer as function of pH

Growth rate and morphology

- An aluminum-containing layer was successfully grown** (Al presence confirmed by EDS)
- Average growth rate of ~4Å/cycle (by measuring layer cross section)
- Non-uniform nucleation** and **"island growth"** suggested by "Bumpy" growth, visible in top-view. (nucleation from specific sites rather than ideal growth of covalently-attached monolayers)



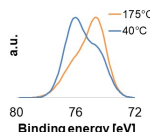
Membrane cross section SEM after 100 ALD cycles



Top-view SEM of membrane after 25 ALD cycles

XPS

Higher defect density in Al_2O_3 grown at lower temperature. could lead to lower density and increased solubility.

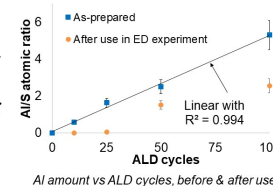


Al_2P peaks for layers grown at 40°C and 175°C

- $\text{Al}2\text{p}$ peak shifted to higher energy indicates more Al-OH and Al-O(OH) bonds.
- Peak deconvolution shows 59% of Al bonds fit Al_2O_3 bonds in layer grown in 175°C vs 35% in 40°C
- O1s peak follows a similar trend
- O/Al ratio is 2.0 in 175°C vs 2.3 in 40°C (1.5 for ideal Al_2O_3)

Stability

- Membranes that were used in Electrodriven ion-transport experiments had consistently lower Al amounts** than before experiment.
- This lack of stability **inhibited further characterization** of the layers deposited on membranes and their functional application.



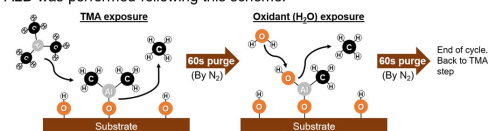
Al amount vs ALD cycles, before & after use

Methods

Atomic Layer Deposition (ALD):

- The Al_2O_3 layer was deposited by alternating exposures to $\text{Al}(\text{CH}_3)_3$ (TMA) and H_2O in the gas phase.
- In ALD, each reactant is supposed to create a covalently-attached monolayer on the surface and is then purged of the reactor.

ALD was performed following this scheme:



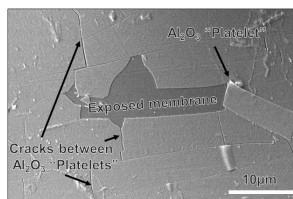
- Al_2O_3 ALD is often performed at elevated temperatures of ~175°C. due to the CEMs sensitivity, the process was performed at 40°C, requiring long purging times between steps.

- The reaction was performed in a Gemstar XT™ benchtop ALD reactor.

Characterization:

- Amount of Al was quantified using EDS. An averaged measurement was taken of a large (μm scale) area, at fixed accelerating voltage of 5keV, which corresponds to a penetration depth of a few microns. Amount of Al was quantified as Al/S ratio, with S present in the membrane.
- ζ potential was measured using a streaming potential method. Measurements were performed using an Anton Paar surPASS² Electrokinetic analyzer using solutions of 0.01M KCl, pH was changed by addition of NaOH and HCl.
- Al_2O_3 layer composition and defects were measured using XPS. Measurements were performed using an ESCALAB 250 XPS/AES on a ~20nm layer of Al_2O_3 . XPS sampled only the layer and not the substrate, verified by lack of Si/Si signal. Peaks in the figure were normalized to the maximum of each peak's counts/s.

What is the mechanism behind the deposited layer's breakdown?



Top-view SEM of membrane after 100 ALD cycles That was wetted & dried again

- Layer cracks and divides into platelets that peel of the membrane surface
- "Platelets" from some wetted samples show a lower Al content than as-prepared membranes.
- No issue with stability appears in layers deposited on a glass substrate

Current hypothesis –

- Peeling occurs due to non-covalent nucleation and weak attachment to surface.**
- Cracks are induced by mechanical stress due to membrane swelling and bending
- Al Traces detected in "exposed" areas could be due to Al_2O_3 penetration into the membrane
- Reduced Al content in some platelets prevents ruling out a dissolution mechanism.

Conclusions

- We performed Al_2O_3 ALD at 40°C.
- The layer deposited had positive surface potential in solution.
- The layer had a significant defect density.
- The layer suffered from lack of stability, possibly due to weak attachment to the membrane surface.

Future plans

- Improve the layer's stability by:
 - Increasing penetration into the membrane by increasing pressure and reactant exposure time
 - Increasing nucleation rates by usage of O_2 plasma as an oxygen source and slightly higher temperatures (<80°C)
- Once stability is improved, we will perform functional (ED) experiments.