Appl. Sci. **2017**, *7*, x; doi: 10.3390/app7080856

Suppressing salt transport through composite pervaporation membranes for brine desalination

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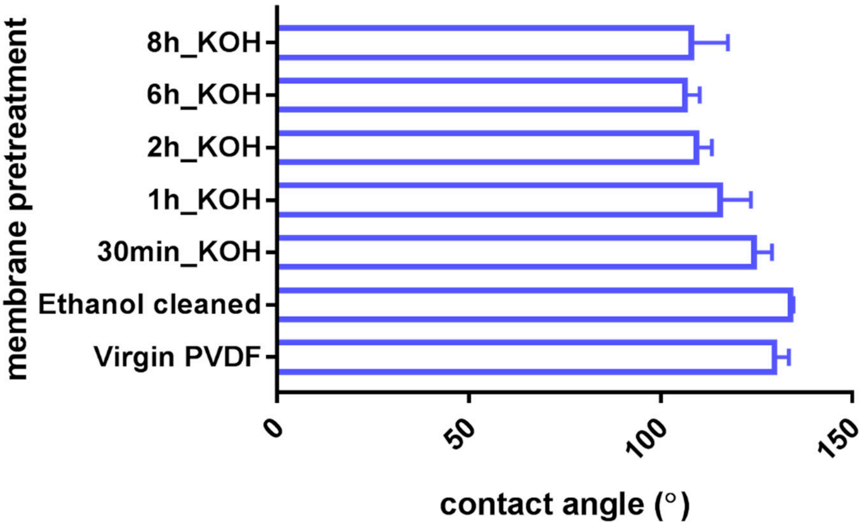

Figure S1. Contact angle after membrane pre-treatment.

Reusability of the composite membrane

One of the main concerns of any water treatment is the issue of consistent performance for long period of time. The reusability of the composite membrane was therefore assessed over several cycles of operation for 100 g/L NaCl solution. The *in-situ* cleaning method was applied by running MIlli-Q water as the feed for a certain period of time after brine wastewater treatment. Two sets of experiments were carried out as shown in **Figure S2**. The 1st set included 24 h on site cleaning with Milli-Q water every 96 hours salt solution test. In the 1st cycle, the flux for a salt solution was 84 % of the pure water flux due to the concentration polarization effect. Subsequently, the flux decreased slowly, however still remained at 71 % of the initial pure water flux, indicating no obvious fouling/scaling during 96 h operation. After switching to Milli-Q water test, the flux value was slightly lower than the initial water flux in cycle 1, due to the residual salt effects. After a 24 h pure water test, the pure water flux reached almost the same value as the initial pure water flux. At the beginning of the 2nd cycle of salt solution test, the flux of more than 80 % of the initial pure water flux was achieved. However, it was found that the flux decline was more obvious than the 1st cycle salt solution test, 62 % of the initial pure water flux was maintained during the operation. A similar trend was observed for the 3rd cycle. From the conductivity profile of the 3 cycles' test, the permeate conductivity was increased with time in all cases. It was also found that for the 2nd and 3rd cycle, the increase of conductivity with time was much faster compared to the 1st cycle; the 3rd cycle exhibited the fastest change.

To simplify the process and study the effect of cleaning on the membrane performance, "23 h salt water + 1 h pure water" cycle test was conducted, as shown in **Figure S2**. For the 2nd and subsequent salt water run, the permeate conductivity started from a value lower than the final value of the previous cycle, but still increased more rapidly. In other words, the 1 h pure water cleaning between brine tests did not change the membrane's swelling, but managed to postpone the rapid increase of permeate conductivity. Compared to the continuous desalination test, the membrane with pure water cleaning between brine tests showed much higher salt rejection efficiency over the whole operation, which indicated that the pure water running has been helpful in removing the residual salt ions in the PVA, recovering the PVA properties to some extent.

However, it was clear that this method did not achieve complete recovery of the membrane. In other words, as the pervaporation process proceeded, it became easier for salt to pass through the membrane, and the ability to reject salt was irreversibly compromised. This irreversible decline in performance was also observed when using PVA for dehydration of alcohol [1]. Some further work is required to provide better cleaning strategies while preserving the stability of PVA layer.

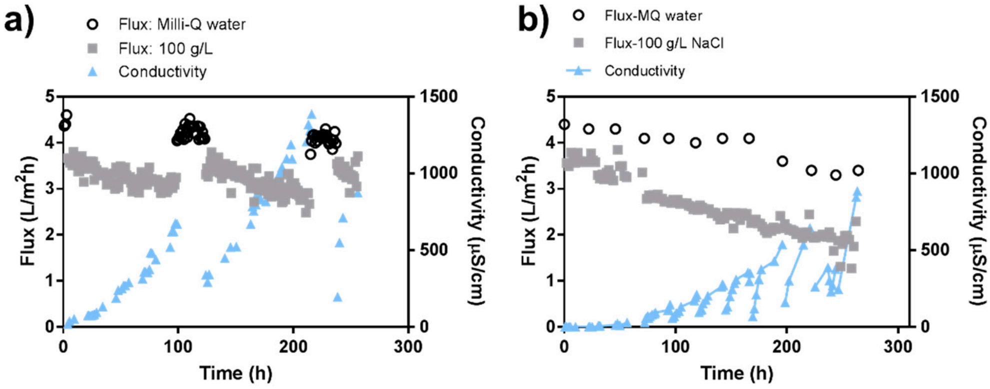

Figure S2. Flux and conductivity profile of composite PVDF membrane with KOH/MR 0.2/5 wt. % by one layer casting, where the membrane was cleaned with *in-situ cleaning* method: (top) "96 h 100 g/L NaCl + 24 h Milli-Q water cycle; (bottom) "23 h 100 g/L NaCl + 1 h Milli-Q water cycle". The feed inlet temperature is 65 ± 1 °C.

Effect of feed concentrations and salt types

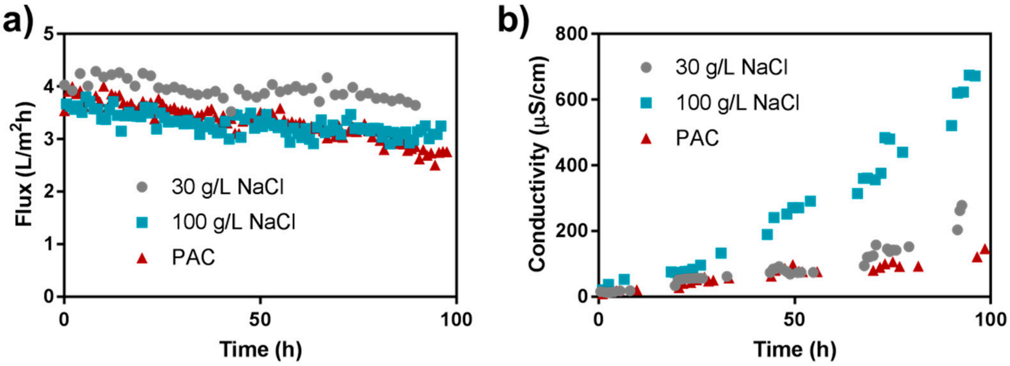

Figure S3. Flux and conductivity profile of composite PVA/PVDF membrane with KOH/MR 0.2/5 wt. % by one layer casting using a feed solution of 30 g/L, 100 g/L NaCl and PAC solution with the same conductivity as 30 g/L NaCl (~55 mS/cm). The feed inlet temperature was 65 ± 1 °C.

We further compared the membrane performance with different concentrated salty solutions. Increased concentration polarization can decrease the driving force across the membrane in the pervaporation process. Moreover, the adsorption of more hydrated salt ions within the PVA matrix can further block the passage of water molecules. As a result, lower water flux and higher permeate conductivity were observed for higher salinity feed solution (**Figure S3**). By monitoring the permeate conductivity using feed with different salinity, i.e., 30, 70, 100, 240 g/L NaCl aqueous solution (results not shown for 70 g/L and 240 g/L NaCl), it was also found that the salt rejection ratio for membrane with the same MR value was constant for different salinity feed solutions at the same operation time. After the first 5 hours operation, an average of more than 99.99 % salt rejection ratio was achieved. The salt rejection ratio was decreased with time, maintaining around 99.6 % for 96 hours operation.

Polyaluminium chloride (PAC) solution with a conductivity of around 55 mS/cm (the same as 30 g/L NaCl) was also used as the feed solution. PAC, as an inorganic polymer, was chosen due to its hydroxyl groups for stronger hydrogen bonding with water molecules than NaCl [2], and its larger size of hydrated ions. As shown in **Figure S3**, the flux decline with PAC was more significant than that of NaCl, which was accompanied by a slower increase of the permeate conductivity. The bulkier PAC hydrated ions transport slower within the PVA layer, and they can more significantly block the passage of water molecules.

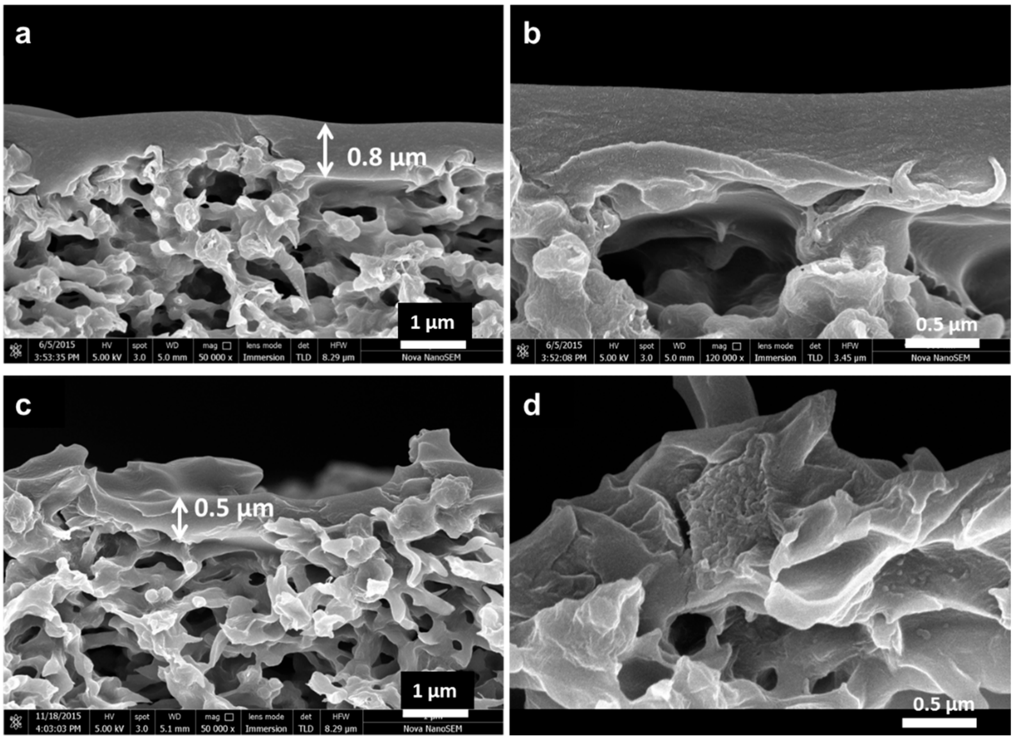

Figure S4. Cross-sectional SEM images of the composite membrane fabricated with the cast coating: **a**) and **b**) PVA/PVDF. **c**) and **d**) PVA0.1GO/PVDF.

Table S1. Contact angles of the composite membrane samples with different GO loadings.

Composite membranes (with PVDF substrate)	Contact angle (°)
PVA/PVDF	30.15±3.5
PVA0.1GO/PVDF	33.72±2.86
PVA0.2GO/PVDF	37.08±2.31
PVA0.3GO/PVDF	31.8±3.07

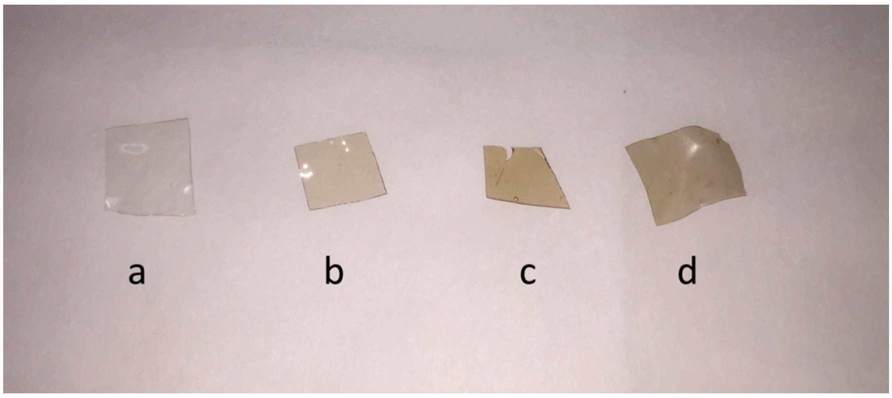

Figure S5. Digital photo of freestanding PVA samples with different GO loadings: **a**) 0. **b**) 0.1 wt. %. **c**) 0.2 wt. %. **d**) 0.3 wt. %.

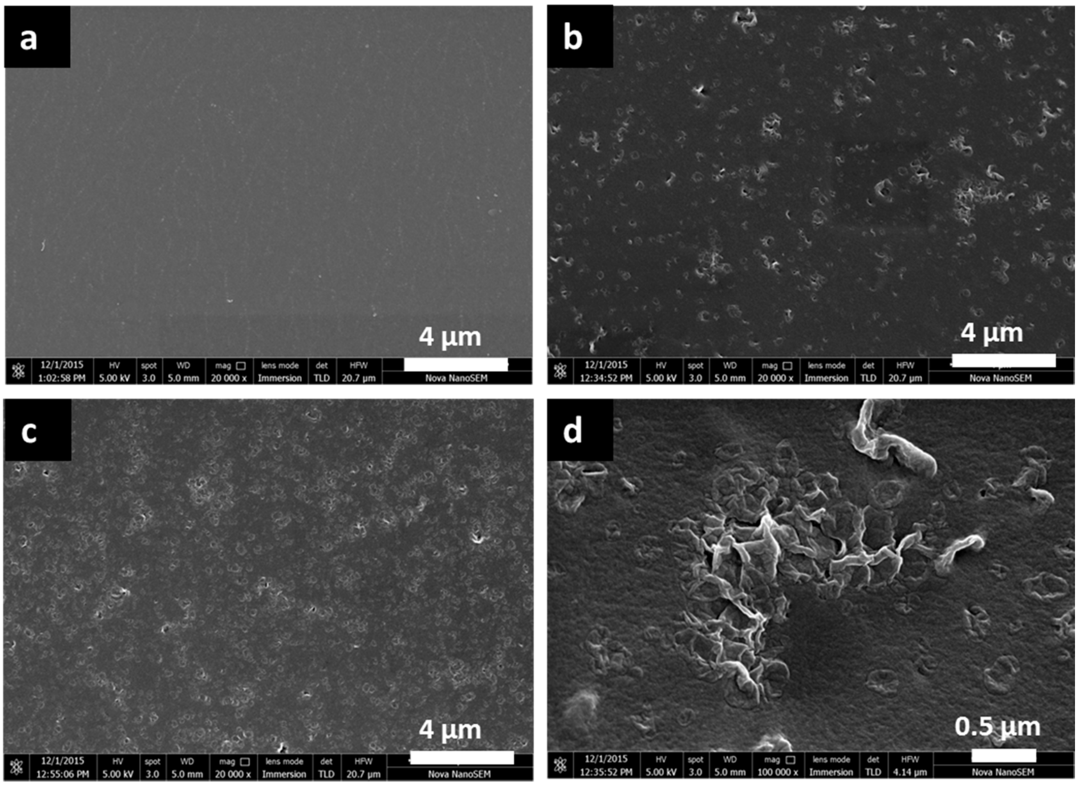

Figure S6. SEM images of freestanding PVA membrane with GO loading of **a**) 0, **b**) 0.1 wt. %, **c**) 0.2 wt. %, **d**) magnified 0.1 wt. %.

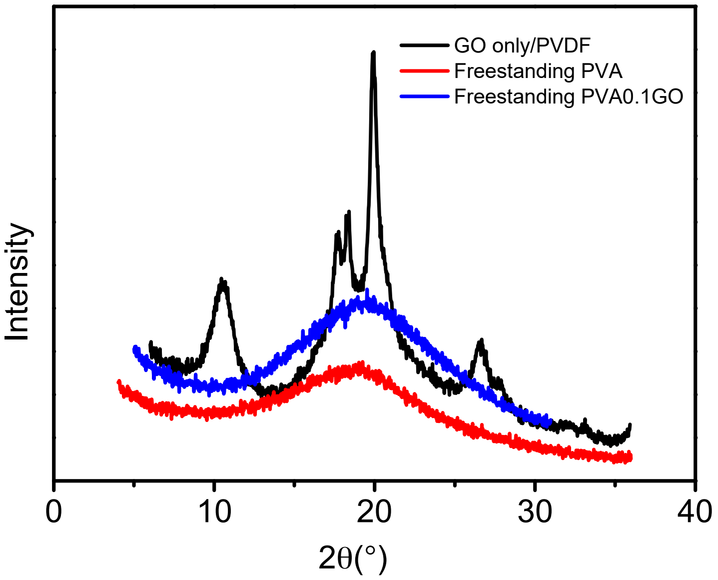

Figure S7. XRD curves of GO only/PVDF, freestanding PVA, and freestanding PVA with GO loading of 0.1 wt. %.

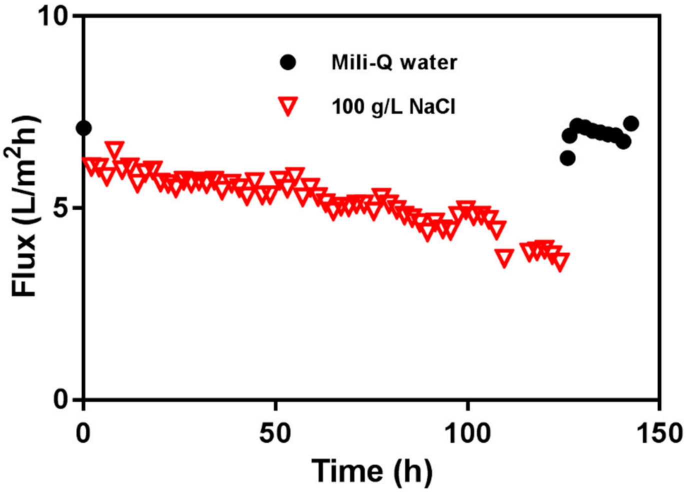

Figure S8. Flux profile of composite membrane PVA0.1GO/PVDF using Milli-Q water, 100g/L NaCl and Milli-Q water as the feed, sequentially.

Reference

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