Supporting Information

Technology-driven Layer-by-Layer Assembly of Membrane for Selective Separation of Monovalent Anions and Antifouling

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1. Theories

1.1. Main theories for selective separation of monovalent anions of anion exchange membranes.

The electrostatic repulsive force between the fixed charges of the membranes surface and ions in solution (Figure S1), and the sieving effect related to the membrane structure and hydrated ionic diameter (Figure S2), and the mobility of different ions (Figure S3) are the main mechanisms of transport and retention for ion exchange membranes with selective separation of ions.

1) The resulting force of anions F was calculated as follows:

F=F'-F"

where F' is the electric field force and attraction of anion exchange membrane; F" is the electrostatic repulsion force of the layer. If F > 0, anions will through the membrane; If F < 0, anions will not through the membrane.



Figure S1. The electrostatic repulsion forces effect for selective separation of monovalent anions. Due to the F (monovalent) > 0, monovalent anions will through; F (divalent) < 0, divalent anions will not through the membrane.

2) The hydrated ion diameter D and membrane pore size Φ ,

If $\Phi > D$, anions through the membrane; If $\Phi < D$, anions will not through the membrane.



Figure S2. The sieving effect of membrane. If the hydrated ion diameter (In practice, the totally ionic hydration energy, hydrogen bond energy and each of the hydrogen bond energy and electric field force will contribute the resulting hydrated ion diameter) lower than the membrane pore size, the anion will through; otherwise, the anion will not through the membrane.

3) The mobility of different ions:

The selective separation of anions may effect by the binding affinity to the fixed ion exchange sites, pH, specific ion channel, etc.



Figure S3. The mobility of different ions. Many reasons contribute the mobility of ions, such as the binding affinity to the fixed ion exchange sites, pH (affect the property of ion exchange membrane), and specific ion channel. For example, if there is ion with a strong the binding affinity to the membrane ion exchange sites, it will easier ion exchange the membrane and through the membrane under the electric field.

1.2. The main theory of reduced for organic fouling property of anion exchange membrane.

The existent of large amount of organic fouling materials could easily coated on the AEMs surface, which reduce the separation effective tremendously and increase the energy consumption in ED. Organic materials are the main fouling for the AEMs surface mostly due to electrostatic attraction and hydrophobic interactions. As shown in Figure S4 and Figure S5, the electrostatic forces of repulsion and hydrophilic materials are the main theories to design the membrane with antifouling property.



Figure S4. (a) Organic fouling materials usually show the negative charge and easily coated the the AEMs surface; (b) The electrostatic forces of repulsion modified on the AEM surface for reduction of negatively charged original materials fouling in ED.



Figure S5. (a) Organic fouling materials usually coated on the hydrophobic membrane surface.(b) The hydrophilic materials modified on the AEM surface for reduction of hydrophobic original materials fouling in ED.

1.3. The theory for stability of functional layers on membrane surface

The stability of layer-by-layer is very important for the resulting membrane. Usually, the heterogeneous layer-by-layer assembly (Figure S6) and the instability between multilayers and original membrane (Figure S7) are the two main reasons of instable layer-by-layer assembled modification layers.



Figure S6. The fluid and electrostatic repulsive force lead the heterogeneous layer-by-layer assembly multilayer easily lose the structure.



Figure S7. Due to the instability between multilayer and original membranes, the fluid will lead them easily lose the structure.

2. Materials.



Figure S8. The chemical structures of poly(4-styrenesulfonic acid-co-maleic acid) sodium salt (PSSMA) (a), 2-hydroxypropyltrimethyl ammonium chloride chitosan (HACC) (b) and 1,4-bis(2',3'-epoxypropyl) perfluoro-1-butane (BEPB)

3. Methods

3.1. Fabrication of the monovalent anions selectivity layers of anion exchange membrane.



Figure S9. Experimental AC assembly technology device for membrane preparation was designed and the details information.

3.2. Measurement of surface electrical resistance.



Figure S10. The membrane surface electric resistance measurement device.



3.3. Selective separation of monovalent anion measurement

Figure S11. The selective separation was measured in a lab design and made device.

3.4. Stability of the membranes measurement.



Figure S12. The scheme of the stability of the membranes measurement.

3.5. Antifouling property evaluation.



Figure S13. The scheme of the antifouling measurement.

4. Results.



4.1. The mass ration of original AEM and AC~LbL#7.5 AEM.

Figure S14. The mass ration of EDS elemental maps of N, S, C, O, F in cross-section by SEM (a) the original AEM and (b) AC~LbL#7.5 AEM.

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