Towards better anion exchange membranes.

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Anion exchange membranes (AEMs) refer to polymers in the membrane shape, having positively charged groups (fixed groups) alongside the polymer chain, which have aroused intense scholar interest. AEMs serve a critical component in various electrochemical systems/devices [1-5]. Currently, increasing the hydroxide conductivity and enhancing the chemical stability of AEMs are the most challenging. Herein, I want to highlight endeavors in fabricating chemically stable and highly conductive AEMs to bring this discussion to a deeper level.

Constructing pendant type AEMs facilitates the formation of micro-phase separated morphology, offers more (or more efficient) hydroxide ion transport "channels" and leads to improved hydroxide conductivity. Micro-phase segregated morphology stems from the enhanced mobility of fixed groups via adding long spacers between the polymer backbone and the fixed groups. Strategies to implement such spacers may include lithiation reaction [6], Friedel-Crafts reaction [7], Suzuki coupling reaction [8] and the more straight-forward Menshutkin reaction [9]. Results suggest that by adding flexible spacers, enhanced phase segregated morphology forms, which consequently leads to increased hydroxide conductivity and suppressed water swelling. An interesting yet to be confirmed fact is that length of the spacers has a distinctive impact on the trend of how obvious an increase in hydroxide conductivity is. Currently, more researchers adopt the act of inducing phase segregated morphology in AEMs by adding flexible spacers. We should also keep in mind that the connection between the polymer backbone and the flexible head groups play an extremely important role in determining the chemical stability of the resulting AEMs [7], especially when an electron-withdrawing effect is concerned [10].

Creating nano-sized hydroxide ion transport channels by stopping the polymers from packing efficiently. By increasing the mobility of the functional groups, driven by the hydrophilicity/hydrophobicity difference they will segregate and form ion transport channels. An extreme situation is to render the AEMs intrinsically micro-porous and all "pores" could serve as ion transport channels, with less resistance. Tröger's base polymers (TB polymers), because of their contorted chain structure, have intrinsic nano-sized pores [11]. We have demonstrated that an unprecedented hydroxide conductivity of 164.4 mS/cm can be attained at a relatively low ion-exchange capacity of 0.82 mmol/g. The results suggest that within the confined space, hydroxide ions exhibit distinctly different transport behaviors as opposed to that in bulk solutions. Similar observations were reported by Prof. Yamaguchi, who found that AEM from a trimethylbenzyl ammonium-appended PIM (polymers of intrinsic micro-porosity) afforded OH- conductivity of 65 m/cm as well as long-term durability [12].

Turing passive hydroxide transport into active transport. Rendering the "fixed" functional groups movable, we have developed AEMs containing mobile ion shuttles via host-guest interactions and disrupting this interaction imparts the side chains with enhanced mobility and increased hydrodynamic radius [13]. The thermally triggered ion shuttling effect endows the polyrotaxane hydroxide conductivity of 180 mS/cm at 90°C, while one remaining challenge is to maintain high OH- conductivity by preventing the diffusion loss of the shuttles under harsh alkali conditions.

Noting that current chemical stability evaluations are ex-situ and totally different from the actual working condition. In a practical AEMFC, the attack of hydroxide ions on AEMs occurs in the absence, or with scarce amount of water. Dekel et al. [14] proved that water molecules have a critical effect on the alkaline stability of quaternary ammonium cations and with increasing amount of water molecules solvating OH- ions, their nucleophilicity and basicity are decreased, leading to slower AEM degradation rate. Therefore, developing standard procedures/methods to make AEM stability assessment approaching the practical working specifications is urgent. Despite of the unresolved challenges, great achievements have been made in designing better AEMs, with both high conductivity and excellent chemical stability.

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