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Designing Advanced Alkaline Polymer Electrolytes for Fuel Cell Applications

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CONSPECTUS

Although the polymer electrolyte fuel cell (PEFC) is a superior power source for electric vehicles, the high cost of this technology has served as the primary barrier to the large-scale commercialization. Over the last decade, researchers have pursued lower-cost next-generation materials for fuel cells, and alkaline polymer electrolytes (APEs) have emerged as an enabling material for platinum-free fuel cells.

To fulfill the requirements of fuel cell applications, the APE must be as conductive and stable as its acidic counterpart, such as Nafion. This benchmark has proved challenging for APEs because the conductivity of OH$^-$ is intrinsically lower than that of H$^+$, and the stability of the cationic functional group in APEs, typically quaternary ammonia ($-NR_3^+$), is usually lower than that of the sulfonic functional group ($-SO_3^-$) in acidic polymer electrolytes.

To improve the ionic conductivity, APEs are often designed to be of high ion-exchange capacity (IEC). This modification has caused unfavorable changes in the materials: these high IEC APEs absorb excessive amounts of water, leading to significant swelling and a decline in mechanical strength of the membrane. Cross-linking the polymer chains does not completely solve the problem because stable ionomer solutions would not be available for PEFC assembly.

In this Account, we report our recent progress in the development of advanced APEs, which are highly resistant to swelling and show conductivities comparable with Nafion at typical temperatures for fuel-cell operation. We have proposed two strategies for improving the performance of APEs: self-cross-linking and self-aggregating designs. The self-cross-linking design builds on conventional cross-linking methods and works for APEs with high IEC. The self-aggregating design improves the effective mobility of OH$^-$ and boosts the ionic conductivity of APEs with low IEC.

For APEs with high IEC, cross-linking is necessary to restrict the swelling of the membrane. In our self-cross-linking design, a short-range cross-linker, tertiary amino groups, is grafted onto the quaternary ammonia polysulfone (QAPS) so that the cross-linking process can only occur during membrane casting. Thus, we obtain both the stable ionomer solution and the cross-linked membrane. The self-cross-linked QAPS (xQAPS) possesses a tight-binding structure and is highly resistant to swelling: even at 80 °C, the membrane swells by less than 3%.

For APEs with low IEC, the key is to design efficient OH$^-$ conducting channels. In our self-aggregating design, long alkyl side-chains are attached to the QAPS. Based on both the transmission electron microscopy (TEM) observations and the molecular dynamics (MD) simulations, these added hydrophobic groups effectively drive the microscopic phase separation of the hydrophilic and hydrophobic domains and produce enlarged and aggregated ionic channels. The ionic conductivity of the self-aggregated QAPS (aQAPS) is three-fold higher than that of the conventional QAPS and is comparable to that of Nafion at elevated temperatures (e.g., greater than 0.1 S/cm at 80 °C).
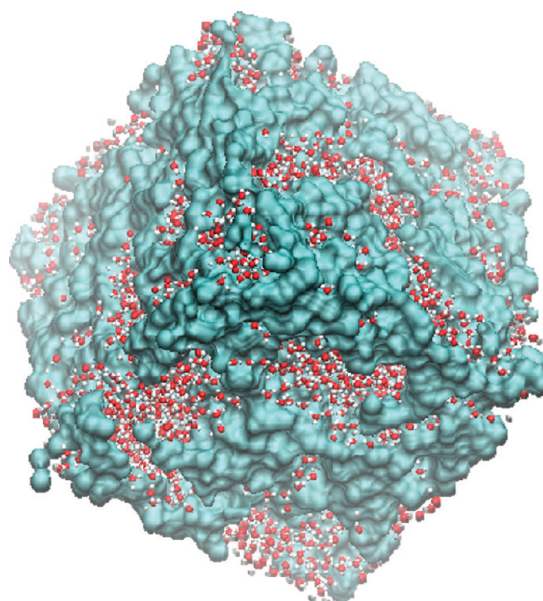
Introduction

Different from the internal combustion engine (ICE), fuel cells convert the chemical energy stored in fuels and oxidants into electricity through electrochemical reactions, which is a quiet, clean, and more efficient fashion of energy conversion, thus being considered as a superior power source

particularly suitable for the future hydrogen-based energy system.[1] In the past decade, electric vehicles powered with polymer electrolyte fuel cells (PEFCs) have been demonstrated worldwide. Despite the great success, this promising technology has not yet met the public's expectations, mostly because of its high cost.

In state-of-the-art PEFCs, the most costly components include the graphite bipolar plate, the perfluorosulfonic acid polymer electrolyte, and the platinum catalyst. The costs of the former two components can, in principle, be well reduced by technological improvements, but the dependence of noble-metal catalysts is rather an issue of resource than just price. The reason that PEFCs have to use Pt catalysts is mainly due to the employment of acidic polymer electrolytes. Specifically, under the harsh condition of the corrosive acid, only noble metals can remain relatively stable. In fact, even Pt is not stable enough under the fuel-cell operating conditions,[2] a worse fact that has been challenging the current PEFC technology.

How about Replacing the Acidic Polymer Electrolyte with an Alkaline One?

To fundamentally get rid of the dependence of Pt catalysts, the fuel cell system needs a revolutionary change, namely, to replace the acidic polymer electrolyte with an alkaline one, because under alkaline conditions some transition metals and metal oxides can serve as stable catalysts for the fuel-cell reactions.[3−7]

Yet the idea of using alkaline electrolytes seems not new at all, as alkaline fuel cells (AFCs) have already been realized and successfully applied in the spaceship a long time before. But things have subtly changed: the desired electrolyte is a polymer version of alkali, rather than the concentrated KOH solution used in AFCs. In an alkaline polymer electrolyte (APE), the cations, typically quaternary ammonia ($-NR_3^+$), are attached onto the polymer chain, and OH^- is the only dissociative ion in the aqueous phase, serving as the charge carrier. Such a seemingly simple change, however, makes things much different. First, because of the use of solid polymer electrolytes, there is no need to worry about the leakage of liquid electrolytes, a severe issue of AFCs in ground applications, where the electrode's waterproofing is always threatened by the carbonate precipitates resulting from the carbonation of KOH solution.[8] The APEs were even found to be tolerant to CO_2.[9,10] Second, by using APEs, there will be "zero gap" between the anode and the cathode since the polymer electrolyte membrane can be made as thin as tens of micrometers, which will lead to a reduction in the

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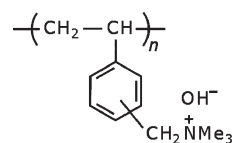
ohmic loss of the cell voltage and thus an improvement in the power density. In summary, the use of APEs is expected to bring a combination of the advantages of PEFCs and AFCs.

The Requirements of Alkaline Polymer Electrolyte (APE) for Fuel Cell Applications

The APE to be applied in fuel cells belongs to the anion exchange resins, traditionally known by the quaternary ammonium polystyrene (Scheme 1), which is, however, not suitable for fuel cells because of the low stability of its functional group[11,12] and the disability of forming a flexible membrane. APEs that satisfy the requirement of fuel cell applications should, at least, possess the following properties:

(1) high ionic conductivity, no lower than 10^{-2} S/cm, expected to be greater than 10^{-1} S/cm.

(2) high chemical and thermal stability under fuel cell operating conditions (e.g., 80 °C).

(3) high mechanical strength and low swelling degree when used in form of flexible membrane, whose thickness is expected to be as small as possible.

(4) capability of being used in the form of solution (called the ionomer solution), so as to facilitate the preparation of polymer impregnated electrodes and the membrane−electrode assembly (MEA).

To the best of our knowledge, there has hitherto been no APE completely fulfilling the above requirements. Therefore, the most important and urgent mission at present is to develop high-performance APEs that fully suit the fuel cell use.

Three Major Approaches for APE Synthesis

In the past decade, there have been literature reports on the synthesis of APEs, which can be categorized into three major approaches:

(1) Physical Grafting. By radiating an existing membrane, reactive radicals are generated on the polymer chains, onto which quaternary ammonia functional groups can then be grafted. Such an approach has been employed by Varcoe, Slade, and co-workers to make APEs based on perfluorocarbon membranes.[13,14] Albeit convenient and clean, this approach seems unable to produce the

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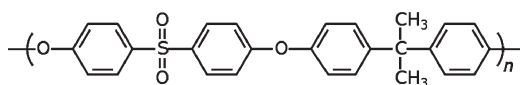
ionomer solution, which then has to be obtained from other approaches when making an MEA.[15,16]

(2) Chemical Grafting. Quaternary ammonia functional groups are grafted, fully through chemical reactions, onto a linear polymer which not only can dissolve in certain solvent (to form the ionomer solution) but also be able to form a strong and flexible membrane. This is an efficient and complete approach that has been widely adopted, such as by our research group and others.[3,17-19] Polysulfone (Scheme 2) and its analogues are the most used polymer backbone, largely because it is a commercially mature product with outstanding stability and capability of forming a flexible thin film with high mechanical strength.

(3) Polymerization. The APE is synthesized, through polymerization reactions, from quaternary ammonia containing monomers.[20,21] The structure of this type of APE is thought to be more designable, and hence, this approach is favored by organic chemists like Coates and co-workers.[22,23] Although this method is able to produce APEs with very high ion-exchange capacity (IEC, the amount of exchange groups per gram of materials), the overall performance of the membrane, in particular, the mechanical strength and the thermal stability, still remains to be further tested.

The Realistic Challenge of APEs

In principle, it should not be difficult to find out, or to design, a stable and flexible polymer backbone, onto which sufficient cationic groups are then grafted so as to attain high ionic conductivity. However, the ionic conductivity of polymer electrolytes is usually gained at the expense of the other aspects of performance, in particular, the mechanical strength and the swelling degree of the membrane.[24] This problem is especially challenging in the APE development.

In comparison to the acidic polymer electrolytes such as Nafion, APEs are thought to be intrinsically inferior in terms of ionic conductivity, because the conductivity of OH^- ($\sigma_{hydroxide}$) is lower than that of H^+ (σ_{proton}) in aqueous phase (for example, in extremely dilute solution, $\sigma_{proton}/\sigma_{hydroxide} = 1.76$).[25] In order to remedy this weakness, it is common sense to design APEs with higher IEC so as to enhance the

OH^- conduction.[17,26-31] However, upon increasing the IEC, the water uptake of APE will become excessive, leading to a significant swelling and a decline in the mechanical strength of the membrane. APEs with high IEC can even dissolve in hot water.[17,28]

To restrict the membrane swelling of APEs with high IEC, cross-linking the polymer chains, or casting the APE onto a supporting mesh, is an effective and commonly adopted solution.[22,29,30] But the cross-linking has sacrificed the solubility of the polymer, thus no stable ionomer solution being available for MEA preparations.[22,29] As for the method of using supporting meshes, it can neither be applied to stabilize the APE in electrodes nor prevent the dissolution of APEs with high IEC at elevated temperatures.

Another solution to the dilemma between ionic conductivity and mechanical stability is to keep the APE at moderate IEC and to enhance the OH^- conducting efficiency, which is thought to be realizable through designing the Nafion-resembling phase-separation structure in APEs.[31,32]

The Strategies for Designing High-Performance APEs

To address the above challenging problem and to design APEs specially tailored for fuel cell applications, we have been testing new APE designs in the past decade. What we try to emphasize in this Account are two strategies that have been proven in our research group to be particularly effective, which are illustrated comparatively in Figure 1. The performance of APE is evaluated here by two key properties: the ionic conductivity and the membrane swelling degree, represented by the horizontal and vertical axes of Figure 1, respectively. Ideal APEs are expected to locate at the right-bottom corner of Figure 1, namely, with high ionic conductivity and low swelling degree.

As mentioned above, although increasing the IEC can enhance the ionic conductivity to some degree, the membrane swelling would become unacceptably enormous. This impractical approach corresponds to the change from (a) to (b) in Figure 1. We have been taking two strategies to address this problem, namely, the self-cross-linking and the self-aggregating, respectively. Strategy 1 is to design a short-range cross-linking mechanism for APEs with high IEC (corresponding to the change from (b) to (c) in Figure 1), such that the cross-linking process can only take place when the polymer chains are in close proximity, a situation that hardly happens in the solution state but occurs upon solidification. Through such a special cross-linking strategy, both the
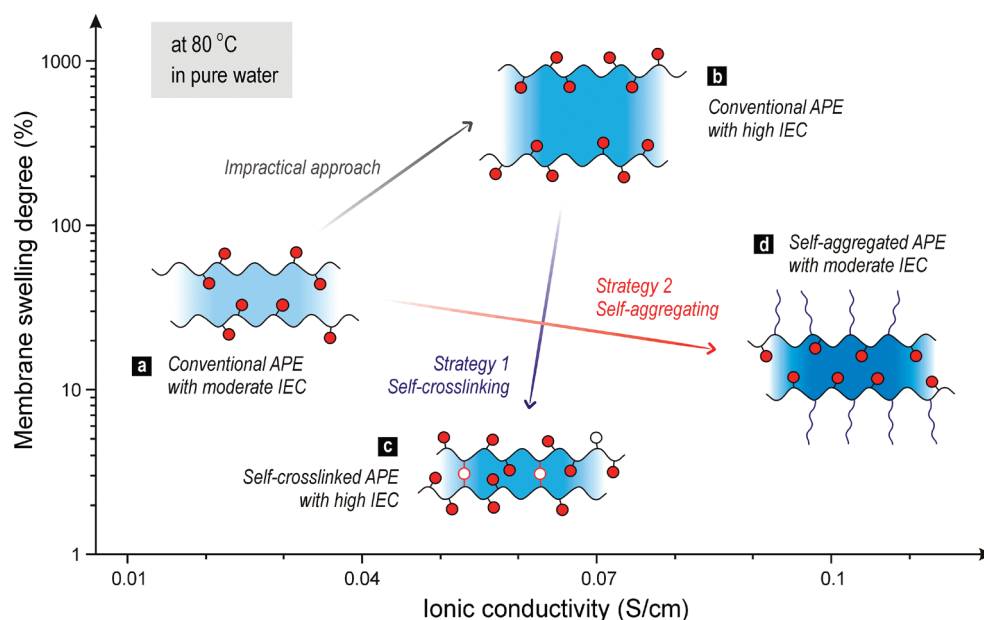
FIGURE 1. Roadmap toward advanced alkaline polymer electrolytes (APEs). To improve the ionic conductivity, increasing the ion-exchange capacity (IEC) is a commonly adopted but impractical approach (from a to b) because of the side effect of severe membrane swelling. Strategy 1 (from b to c) is to develop a short-range cross-linking mechanism, such that the membrane swelling of APEs with high IEC can be greatly reduced due to the thus-formed tight-binding structure, while the ionomer solution can remain stable before solidification. Strategy 2 is to design additional hydrophobic side-chains onto the backbone of APEs with moderate IEC (from a to d), so as to drive the microscopic hydrophilic/hydrophobic domain separation and to cause the aggregation of ionic channels, thus enhancing the OH^- hopping conduction.
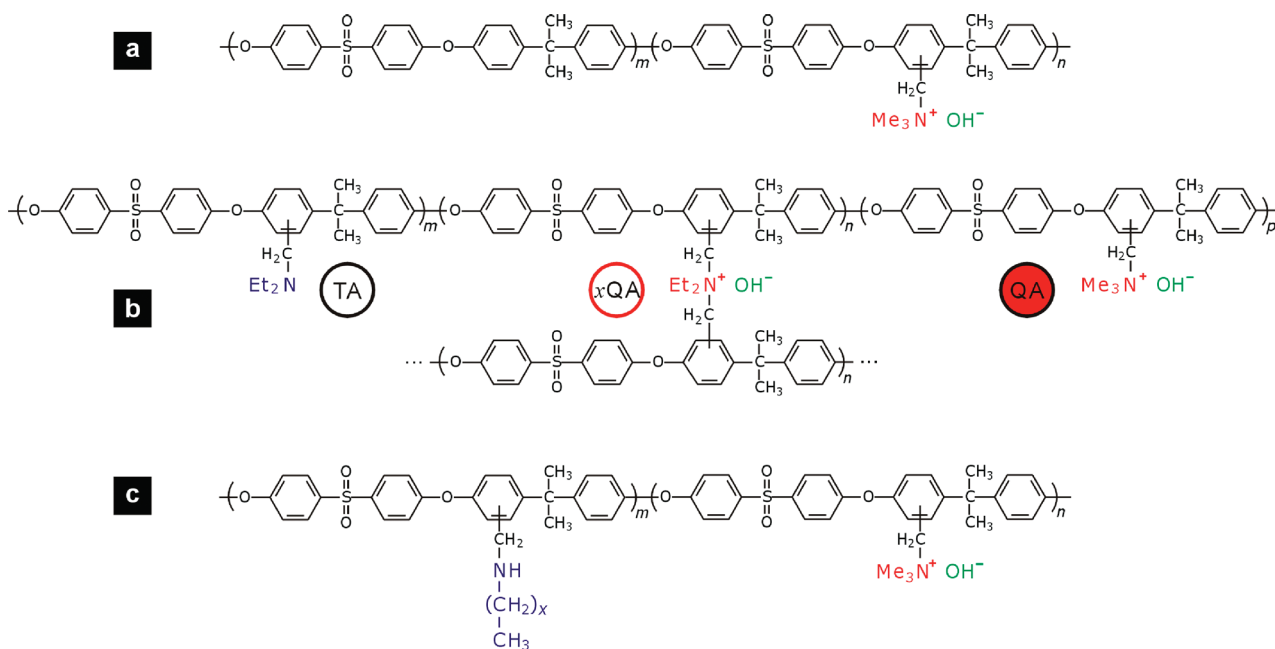

FIGURE 2. Illustrations of the molecular structures of APEs discussed in this paper. (a) Quaternary ammonia polysulfone (QAPS), (b) self-cross-linked QAPS (denoted as *x*QAPS), and (c) self-aggregated QAPS (denoted as *a*QAPS).

ionomer solution and the tightly cross-linked membrane can be obtained, thus removing the side effect of conventional cross-linking methods and suppressing significantly the membrane swelling of APEs with high IEC.

Strategy 2 takes a fundamentally different approach: it starts from APEs with moderate IEC so as to prevent excessive membrane swelling and then designs additional hydrophobic side-chains to drive the aggregation of hydrophilic

domains (corresponding to the change from (a) to (d) in Figure 1), such that the local ion concentration will increase and the hopping conduction of OH$^-$ can be effectively enhanced. As to be seen, such a self-aggregating strategy can dramatically boost the ionic conductivity of APEs to reach 0.1 S/cm at 80 °C.

Implementations for the Self-Cross-Linking and Self-Aggregating Design of APE

Both the above strategic designs of advanced APEs can be realized by a structural modification of the quaternary ammonia polysulfone (QAPS, Figure 2a), a conventional APE that has been achieved in our previous studies.[4,17] The synthesis of QAPS involves two major steps: (1) The polysulfone backbone is grafted with chloromethyl groups to produce a reactive intermediate (Figure S1a, Supporting Information), denoted as CMPS. (2) The CMPS then reacts with the trimethylamine to produce the chloride form of QAPS. After replacing the Cl$^-$ with OH$^-$, the final form of QAPS results. The grafting degree of chloromethyl groups in the first step is controllable in our synthetic method, and has mostly determined the IEC of the resulting QAPS.

To realize the self-cross-linked QAPS (denoted as *x*QAPS), an additional synthetic step is introduced: before the CMPS is exposed to trimethylamine, a certain amount of diethyl-amine is added to produce tertiary amino groups (−NEt$_2$, TA) on the polysulfone backbone (Figure S1b, Supporting Information), and then the TA-containing CMPS is further functionalized with the quaternary ammonia group (QA), resulting in a TA-containing QAPS (Figure 2b). The TA possesses a low reactivity in solution at room temperature, but can react with the residual chloromethyl group on neighboring polysulfone chains in close proximity during membrane casting (Figure 2b). Thus, such a special form of QAPS can either remain soluble in form of solution or become cross-linked upon solidification.[30]

The implementation of self-aggregated QAPS (denoted as *a*QAPS) is similar to that of *x*QAPS, except that the polysul-fone backbone is not additionally grafted with TA but with long alkylamine chains. Specifically, before the QA genera-tion step, a certain amount of primary alkylamines with long hydrophobic chains, such as 1-hexanamine, is introduced to react with the CMPS (Figure S1c, Supporting Information); then the remaining chloromethyl is fully converted to QA (Figure 2c). The use of primary alkylamines, rather than secondary ones, makes the grafting reaction much easier, as the reactivity of long alkylamines is relatively low.
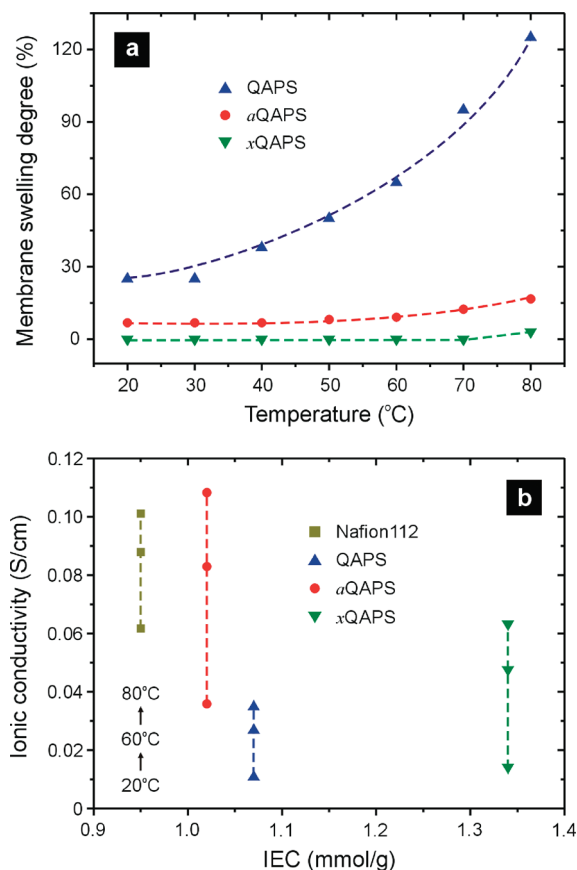

FIGURE 3. Performance improvement upon structural modifications. (a) The membrane swelling can be effectively suppressed through either self-cross-linking or self-aggregating; the swelling degree of *x*QAPS membrane is less than 3% even at 80 °C. (b) The ionic conductivity can be improved by increasing the IEC (in the case of *x*QAPS) or, more effectively, through aggregating ionic channels (in the case of *a*QAPS). At elevated temperatures, the ionic conductivity of *a*QAPS is compar-able to that of Nafion.

The resulting hydrophobic side-chains can hardly be regarded as a functional group in this case, but they actually impose a great impact on the structure and property of the *a*QAPS membrane, as to be revealed in the following sections.

The Remarkable Performance of *x*QAPS and *a*QAPS

Although only are small structural modifications made in the transformation from QAPS to *x*QAPS and *a*QAPS, the result-ing performance improvements turn out to be remarkable. Figure 3a demonstrates the distinct change in the tempera-ture-dependent membrane swelling degree. For the con-ventional QAPS, even its IEC is controlled to be moderate (1.07 mmol/g); the membrane still swells over 25% at room temperature and expands significantly with increasing the temperature. Such an unacceptable swelling behavior has

been suppressed, to a great extent, by the effective structural design of *x*QAPS and *a*QAPS. For the *a*QAPS with moderate IEC (1.02 mmol/g), its membrane swelling degree remains below 10% at room temperature and increases only slightly with temperature. The most surprising effect is caused by *x*QAPS: albeit with a high IEC (1.34 mmol/g), it does not swell at all at temperatures below 80 °C; and even at 80 °C, the membrane swelling degree is less than 3%. Such a highly antiswelling property can only be ascribed to the tight-binding structure of the *x*QAPS membrane.

In comparison to the QAPS, the *x*QAPS possesses a higher IEC, which should lead to an obvious increase in the ionic conductivity. As revealed in Figure 3b, however, the ionic conductivity of *x*QAPS is only slightly higher than that of QAPS at room temperature, suggesting that the tight-binding structure has significantly reduced the water uptake and thus restricts, to some extent, the ionic conduction. But upon increasing the temperature, the ionic conductivity of *x*QAPS increases faster than that of QAPS, manifesting the benefit of high IEC. The most intriguing observation in Figure 3b is the striking improvement in the hydroxide-conducting effi- ciency of *a*QAPS. Albeit with the lowest IEC, the ionic con- ductivity of *a*QAPS is 3-fold higher than that of QAPS and *x*QAPS at room temperature, clearly indicating that the OH$^-$ conduction in *a*QAPS is of a much higher efficiency. Further- more, the ionic conductivity of *a*QAPS increases largely with temperature and becomes comparable to, or even slightly higher than, that of Nafion at elevated temperatures, for instance, reaching 0.11 S/cm at 80 °C. Such an outstanding hydroxide-conducting behavior is due to the superior struc- tural design of *a*QAPS, which also implies that high IEC is not a necessary condition for achieving the high ionic conduc- tivity of APE, the structural factor could be more determining.

Note that the ionic conductivity of polymer electrolytes (including APEs and Nafion) is measured in our works using the two-probe AC impedance method rather than the four- probe one[22,23] which is thought to have overestimated the ionic conductivity. Also worth mentioning is that the super- ior performance gained by *x*QAPS and *a*QAPS is lasting at elevated temperatures. During a test in 90 °C water, both the mechanical strength and the ionic conductivity of *x*QAPS and *a*QAPS membranes show no sign of degradation over 1000 h.

Experimental Proofs for the Structural Feature of *x*QAPS and *a*QAPS

It is interesting to see the peculiarities exhibited by *x*QAPS and *a*QAPS: the *x*QAPS is exceptionally antiswelling even with a
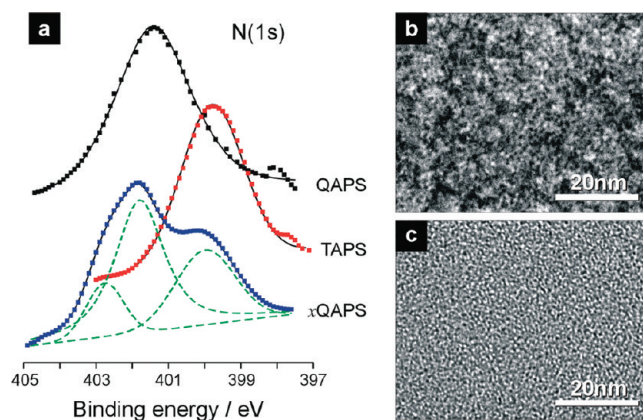
FIGURE 4. Experimental characterizations for the key structural feature of *x*QAPS and *a*QAPS. (a) XPS evidence for the existence of three types of amino group in *x*QAPS. XPS spectra of QAPS and tertiary amino polysulfone (TAPS) are also presented for reference. (b) Transmission electron microscopy (TEM) image of *a*QAPS membrane dyed with I$^-$, manifesting the aggregation of the hydrophilic domains (dark spots) and the enhanced microscopic phase separation. (c) A TEM image of QAPS membrane dyed with I$^-$, showing the uniform distribution of the hydrophilic/hydrophobic domains with relatively smaller size.

high IEC, while the *a*QAPS is highly conductive just at a moderate IEC. These unusual behaviors are the consequence of the structural modifications on conventional QAPS (Figure 2), guided by the aforementioned strategies (Figure 1). The self- cross-linking feature of *x*QAPS is implemented by deliberately replacing a part of the QA group with a TA group, which can then react with the residual chloromethyl group on neighboring backbones to form a cross-linking QA group (denoted as *x*QA, Figure 2b). Thus, in an *x*QAPS membrane, there are three types of amino groups (QA, TA, and *x*QA), and the formation of *x*QA is a key structural feature. We have employed X-ray photoelectron spectroscopy (XPS) to ascertain the existence of three different amino groups in *x*QAPS.[30] As revealed in Figure 4a, the binding energy (BE) of the N 1s electron differs clearly between the QA in QAPS and the TA in tertiary amino polysulfone (TAPS), a QA-free polymer deliber- ately prepared for reference. It is understandable that, being a cation, the QA has a greater BE (~402 eV) than that of the TA (~400 eV). As for the *x*QAPS, its XPS signal is clearly composed of three peaks, with the two low-BE ones corresponding to the QA and the TA, respectively; and the new peak emerging at around 403 eV can only be attributed to the generation of *x*QA. The greatest BE associated with *x*QA is probably because of the enhanced electron-withdrawing effect of the two benzyl groups in proximity.[33]

For the *a*QAPS, the addition of long alkyl side-chains (Figure 2c) is expected to enhance the microscopic phase separation between hydrophilic and hydrophobic domains
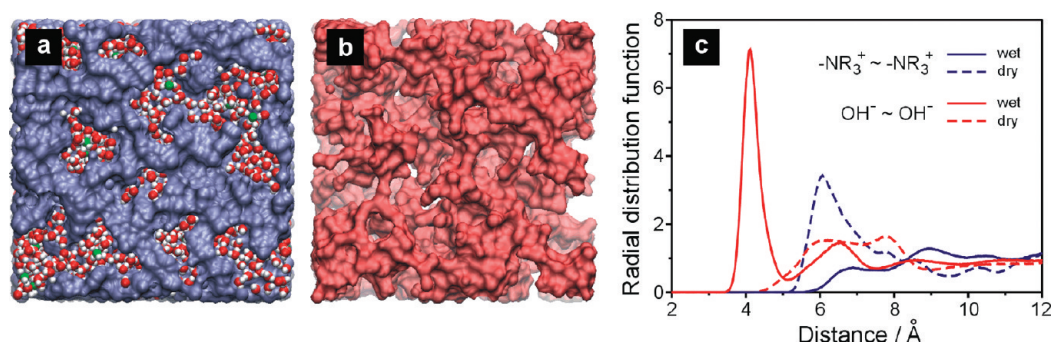
FIGURE 5. Molecular dynamics (MD) simulations for the structure of hydrated aQAPS ($\lambda = 30$). (a) A view of the simulated hydrophilic/hydrophobic domain separation: the hydrophilic domains that contain water molecules (represented by red-white balls) and OH$^-$ (represented by green-white balls) are intercalated in the hydrophobic network formed by the polysulfone backbone and the alkyl side-chains (represented by the blue continuum). (b) Another view of (a) with the hydrophobic network being hidden and the hydrophilic domains being represented in continuum mode so as to see the interconnections between aqueous clusters. (c) The radial distribution function (RDF) of the $-$NR$_3^+$ and the OH$^-$ in wet and dry aQAPS membranes, based on which the aggregation of OH$^-$ upon hydration is evident.

in the membrane, such that the OH$^-$ will locally aggregate and the OH$^-$ hopping conduction can become more effective. Thus, the enhanced hydrophilic/hydrophobic domain separation is a key structural feature of aQAPS. To unravel this microscopic characteristic, aQAPS and QAPS thin films are cast onto a Cu grid, followed by exchanging the anions in both films for I$^-$, and then subjected to transmission electron microscopy (TEM) observations. As manifested in Figure 4b and c, whereas the hydrophilic (dark spots) and hydrophobic (light spots) domains in conventional QAPS seem rather small and distribute in a uniformly mixed pattern (Figure 4c), the hydrophilic/hydrophobic domains in aQAPS are bigger in size and distribute in an aggregated pattern (Figure 4b). Furthermore, it is not difficult to find the interconnections among the aggregated hydrophilic domains. In other words, Figure 4b provides clear and compelling evidence for the structural peculiarity of aQAPS: upon introducing the hydrophobic side-chains, the OH$^-$ containing hydrophilic domains are driven to aggregate to each other, forming larger and more efficiently interconnected ionic channels. We think it is such a superior structure that renders aQAPS highly efficient of OH$^-$ conduction.

Structural Insights from Molecular Dynamics Simulations

The above-observed aggregation structure of hydrophilic domains in aQAPS resembles, to large extent, the well-known Gierke model proposed for reasoning the highly efficient proton conduction in Nafion.[34] Yet the molecular structure of aQAPS is quite different from that of Nafion: for aQAPS, the hydrophilic QA groups are closely attached on the relatively rigid polysulfone backbone, which equips separately with hydrophobic alkyl side-chains; while for Nafion, the hydrophilic sulfonic groups are positioned at

the end of the long, flexible, hydrophobic side-chains grafted on the polytetrafluoroethylene (PTFE) backbone. It seems that the mechanism of forming the hydrophilic/hydrophobic domain separation should be different for these two distinct polyelectrolytes.

In order to gain molecular insights into the microscopic morphology of aQAPS, a series of molecular dynamics (MD) calculations have been performed using methods similar to the structural simulation of Nafion,[35−37] and typical results of fully hydrated aQAPS are exemplified in Figure 5. Figure 5a is a representative view of the simulated hydrophilic/hydrophobic separation morphology, showing that the OH$^-$ containing water clusters are intercalated in the hydrophobic network formed by the polysulfone backbone and alkyl side-chains. The aqueous clusters in aQAPS are smaller in size than that in Nafion,[34] but well connected to each other at sufficient hydration level, as illustrated in Figure 5b.

In addition to the observation of well-established ionic channels in aQAPS, MD simulations have also found important evidence for the aggregation of OH$^-$ in hydrated aQAPS. According to the radial distribution function (RDF) analysis (Figure 5c), the OH$^-$ is found to be significantly aggregated upon hydration, indicating that the OH$^-$ is strongly solvated and dissociated far away from the cationic group. Such an aggregation effect, however, is not seen for the QA functional groups which are still closely bound to the rigid backbone. Thus, the mechanism of forming hydrophilic/hydrophobic domain separation in aQAPS might be fundamentally different from that in Nafion. In the case of Nafion, the separated, broad hydrophilic domains are thought to form through the organization of loose side-chains and the aggregation of sulfonic functional

groups.[38] While in the case of *a*QAPS, the formation of ionic channels does not rely on the organization of QA functional groups, but on the dissociation of hydrated OH⁻ into the free space in *a*QAPS. Such free spaces are small and uniformly distributed in conventional QAPS, but enlarged and aggregated in *a*QAPS because of the loose and random stack of the backbones with long side-chains. Nonetheless, the introduction of long, hydrophobic side-chains does cause an enhancement in the microscopic phase separation between the hydrophilic and hydrophobic domains, which is in line with the original design strategy for *a*QAPS.

Conclusions and Perspective

In principle, there are two major approaches to improving the ionic conductivity of alkaline polymer electrolytes (APEs): (1) increasing the ion-exchange capacity (IEC) of the polyelectrolyte and (2) increasing the effective mobility of the charge carrier (OH⁻). While the first approach seems relatively easier to be realized, the second one requires superior design of the ionic channels in the polymer. In reality, the first approach turns out not to be as simple as expected; the APE will absorb excessive water when increasing the IEC, leading to a severe membrane swelling and mechanical-strength decline. To address the problem, making cross-linked APE membrane is a usually adopted measure, but it leaves the ionomer solution unavailable for PEFC assembling.

Our strategy for solving the problem of the first approach is to design a "smart" cross-linking mechanism: the cross-linking process will not happen when the APE is in solution state but occur upon solidification, such that the ionomer solution and the cross-linked APE membrane can both be obtained. Such a strategy has been realized in our research group by designing the self-cross-linked quaternary ammonia polysulfone (*x*QAPS), in which the tertiary amino group acts as a short-range cross-linker and can bind with neighboring polymer backbones in close proximity. The resulting tight-binding structure renders the *x*QAPS exceptionally antiswelling, with its swelling degree being less than 3% at 80 °C.

To further enhance the ionic conductivity of APEs, we have focused on designing efficient ionic channels for OH⁻ conduction, namely, taking the aforementioned second approach. Our strategy is to design additional hydrophobic side-chains to drive the microscopic phase separation and the aggregation of ionic channels. Such a strategy has been realized in our research group by designing the self-aggregated quaternary ammonia polysulfone (*a*QAPS). Both the experimental characterization and the molecular dynamics (MD) simulation have revealed that the ionic channels are enlarged and aggregated in *a*QAPS. This superior structure makes the *a*QAPS as conductive as Nafion at fuel-cell operating temperatures; for example, its ionic conductivity is greater than 0.1 S/cm at 80 °C.

By now, we think we have successfully passed the first phase of the development of advanced APEs. Through the self-cross-linking and the self-aggregating approaches presented in this Account, APEs can now be made as good as the acidic polymer electrolyte in terms of the ionic conductivity and the dimensional stability of membrane, which have fulfilled the basic requirements of fuel cell applications. Yet there are still challenges for APEs to become completely suitable for real applications. For instance, the oxidative degradation of APEs under fuel-cell operating conditions has been a concern; how to enhance the oxidation tolerance of APEs remains an open subject. Replacing the QA with other functional groups could be a solution.[3,39] Relevant first-principles calculations are underway in our research group with attempts to identify the possible structural weakness and to find out the resolution.

Supporting Information. Supplementary figure and experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

BIOGRAPHICAL INFORMATION

Jing Pan obtained her B.S. (2006) degree from Wuhan University and is currently in her last year as a Ph.D. candidate in Prof. Zhuang's group. Her research interest and most efforts have been focusing on developing novel alkaline polymer electrolytes and their application in fuel cells.

Chen Chen obtained his B.S. (2005), M.S. (2007), and Ph.D. (2011) degrees from Wuhan University in Prof. Zhuang's group and is currently a postdoctoral fellow there. His research interest is micro- and mesoscale simulation of polyelectrolytes and the rheological behavior of confined fluids.

Lin Zhuang earned his Ph.D. (1998) in electrochemistry at Wuhan University, after then he joined the Department of Chemistry at Wuhan University and became a full professor in 2003. He was a research scholar at Cornell University (2004−2005). He has been working on fuel cell catalysis and materials.

Juntao Lu graduated from Wuhan University in 1963 and has been working there since. He visited Case Western Reserve University

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FOOTNOTES

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