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Highly hydroxide conductive ionomers with fullerene functionalities†

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A novel ionomer was designed that will not poison the catalyst in alkaline fuel cells, by incorporating for the first time *N*-methyl pyrrolidine- C_{60} cation in polymeric anion exchange ionomers. The resultant fullerene-based anion exchange ionomer shows an extremely high hydroxide conductivity (182 mS cm^{-1}) at a low cation concentration (0.62 mmol g^{-1}).

The alkaline polymer electrolyte fuel cell (APEFC) has aroused tremendous research interest as an efficient energy conversion device because of its faster oxygen reduction reaction (ORR) kinetics, the utilization of metals which are abundant in the earth, easy water management, the adoption of high energy density liquid (such as methanol, hydrazine), and so on. The most crucial component in the APEFC system is an anion exchange ionomer (AEI), which acts as either an anion exchange separator between electrodes or as binders in the membrane electrode assembly (MEA). Currently, the major challenge in developing applicable AEIs for high performance APEFC includes the following aspects: (1) construction of highly hydroxide conductive AEI for enhanced energy efficiency and current density. (2) Eliminating the poisoning of cationic head groups in AEI on ORR catalysts. To minimize the ionic resistance in the catalyst layer of the electrode, AEI and the catalyst should be in intimate contact. Thus, the effect of the AEI cationic groups on the performance of the catalyst is of critical importance. For example, the imidazolium groups fundamentally change the mechanism of ORR on the polycrystalline platinum (Pt) catalyst and the presence of a benzene ring in close proximity to quaternary ammonium groups also had a negative effect on ORR.¹ A detailed study on the effect of various cationic groups (such as quaternary trimethyl ammonium groups, caged quaternary ammonium groups, imidazolium groups and phosphonium groups) on ORR reveals that small concentrations of such

cationic species can seriously inhibit Pt/carbon (C) catalytic activities in high pH aqueous electrolytes. The presence of imidazolium species gave particularly severe reductions in catalytic performances.² Gu *et al.* found that phosphonium groups tend to be preferentially adsorbed on the catalysts [silver (Ag)] surface, leading to catalyst poisoning.³ (3) When AEI and ORR catalysts are in close contact to each other, the match between the electron transfer pathway and the hydroxide conductive pathway becomes especially important. In conventional MEA configuration, the electron transfer and the hydroxide conductive pathways are separated. Electrons are transferred by the catalyst (in most cases, C supported nano catalyst), whereas hydroxides are conducted *via* AEI. Provided the catalyst is completely wrapped by the AEI, the internal resistance of such a configuration is high. Well-defined interfacial structure leads to excellent electron and hydroxide transfer and realizes a high fuel-cell performance.⁴

To conquer such challenges, it is intended that a unique type of AEI with a highly hydroxide conductive capacity is developed, which can bridge the transfer of electrons and conduction of hydroxide (possibly with ORR activity). It is supposed to be utilized as a binder in APEFC. Compared with conventional binders, this novel ionomer binder can facilitate the transport of OH^- (generated at the cathode *via* ORR) from the catalyst layer to the cell compartment because of its higher hydroxide conductivity. In the meantime, the catalytic activity enables the ionomers to acquire the ability to be involved in ORR. In this way, the internal resistance in the MEA can be greatly reduced.

To acquire ORR catalytic activity, the functional groups in the ionomers have to be involved in the electron transfer chain of the cathode reaction and it should possess the ability to interact with or capture electrons (e^-). Inspired by the commercial utilization of [6,6]-phenyl- C_{61} -butyric acid methyl ester (PC_{61}BM) as an electron acceptor in organic solar cells, C_{60} derivatives were selected for this work. Fundamentally, C_{60} behaves like an electron accepting molecule and is able to accept up to six electrons in solution.⁵ This offers the unique opportunity for C_{60} (derivatives) to be involved in ORR. However, it is difficult for the captured electrons in C_{60} to escape because of the symmetric

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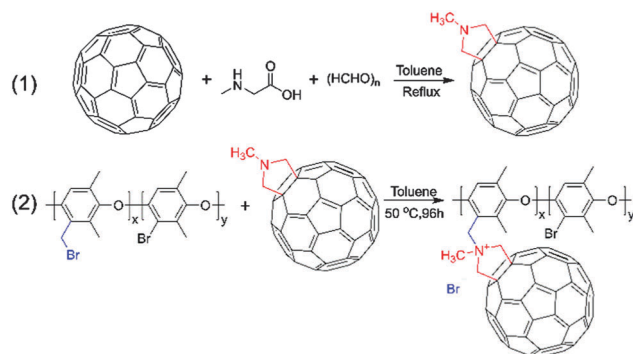


Fig. 1 (1) Synthesis of *N*-methyl pyrrolidine- C_{60} (MPC₆₀), (2) preparation of AEI based on brominated poly(2,6-dimethyl-1,4-phenylene oxide) (BPPO) and pyrrolidinium cations.

chemical structure of C_{60} . Therefore, asymmetry needs to be created. It is similar to the case of “point discharge”. To date, fullerene chemistry is an active field and many reactions are available for molecular modification.⁶ In this research the Prato reaction was incorporated⁷ to create asymmetry for electron transfer and to add functionality (pyrrolidine) to make an AEI. The realization of hydroxide conductivity can then be fulfilled by converting the resulting pyrrolidine into pyrrolidinium.

Fig. 1 presents the overall reaction scheme to prepare such a novel AEI. It should be mentioned that series of chloromethylated or brominated polymers can be incorporated in this synthetic procedure. Brominated poly(2,6-dimethyl-1,4-phenyleneoxide) (BPPO) was chosen as the polymer scaffold because of its easy accessibility. The structure of the synthesized *N*-methyl pyrrolidine- C_{60} (MPC₆₀) was confirmed using nuclear magnetic resonance (NMR) spectroscopy (Fig. S1, ESI†). MPC₆₀ was reacted with commercial BPPO to form an AEI (BPPO-MPC₆₀, Fig. S2, ESI†) with pyrrolidinium head groups. The titrated ion exchange capacity (IEC) of the resulting AEI is 0.62 mmol g⁻¹. This indicates the successful grafting of fullerene pyrrolidine onto the backbone of BPPO. The theoretical IEC value of the BPPO-MPC₆₀ membrane is 0.82 mmol g⁻¹ when all the benzylic bromides are converted into pyrrolidinium cations. As well as the titration deviation, the difference in titrated IEC and theoretical IEC is attributed to the incomplete transformation of benzylic bromides. The incomplete transformation stems from the steric hindrance of MPC₆₀ in the Menshutkin reaction (Fig. 1(2), the reaction to form pyrrolidinium cations). The residual benzylic bromide groups can be further transformed into cationic functionalities by simply immersing the ionomers in aqueous trimethylamine aqueous solution. However, this transformation was not conducted to investigate solely the effect of MPC₆₀ functionality.

The hydroxide conductivity of the BPPO-MPC₆₀ ionomer at 30 °C is 86.01 mS cm⁻¹ (Fig. 2). In fuel cell systems, a higher operating temperature results in a higher catalyst activity and less bicarbonate formation, which shows intrinsic lower mobility than OH⁻ (mobility: OH⁻ = 4.26 HCO₃⁻).⁸ When the operating temperature is elevated, an increase in hydroxide conductivity is observed. At 80 °C, the hydroxide conductivity of

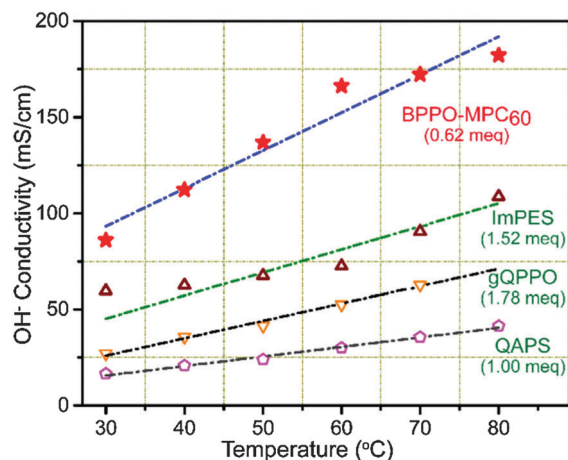


Fig. 2 Hydroxide conductivities of the BPPO-MPC₆₀ anion exchange ionomer at varied operational temperatures and a comparison of hydroxide conductivities with typical ionomers.

the BPPO-MPC₆₀ ionomer reaches up to 182.13 mS cm⁻¹. To fabricate a highly efficient APEFC, ionomers with OH⁻ conductivities higher than 100 mS cm⁻¹ are crucial. From this perspective, the ionomer prepared in this research shows great potential for further applications. The hydroxide conductivity of the BPPO-MPC₆₀ ionomer was compared with some of the prevailing AEIs. The hydroxide conductivity of the BPPO-MPC₆₀ ionomer at 60 °C is 166.26 mS cm⁻¹, which is 2.3 times that of imidazolium functionalised poly(ether sulfone) (ImPES),⁹ 3.2 times that of grafted poly(phenylene oxide) (gQPPO)¹⁰ and 5.5 times that of quaternary ammonium polysulfone (QAPS).¹¹ Compared with ionomers with specially designed architectures, the hydroxide conductivity of BPPO-MPC₆₀ membrane at 60 °C is about twice that of aQAPS-S8,¹¹ in which an ionic highway is formed because of the well-designed architecture. Comparatively, the easy preparation of the ionomer developed in this research is one advantage over preparation of conventional ionomers. Most importantly, no conductivity can be observed when the ionomer is dehydrated (in dry state), indicating no electron transfer. This means that the conductivity attained in humid conditions arises from the conduction of hydroxide ions.

The highly conductive nature of the BPPO-MPC₆₀ ionomer might stem from the “huge” size of the cationic head groups. The diameter of the C_{60} molecule is around 0.71 nm, which is much larger than the conventional ammonium cations, even the steric crowded phosphonium cations.¹² The distance between the BPPO chains is increased because of the incorporation of huge C_{60} molecules. Therefore, the polymer backbone cannot be packed efficiently, in which case a sub-nano “cavity” could be formed. This in turn results in an increased free volume inside the polymer matrix. Because of the hydrophilicity of the pyrrolidinium cations, these sub-nano cavities are surrounded by water molecules in a humid environment. Correspondingly, the increase in free volume adds more hydroxide conductive channels. This explains why such high hydroxide conductivity is obtained considering the relatively low ion exchange capacity. From this point of view, it is envisaged that polymers with intrinsic micro-porosity

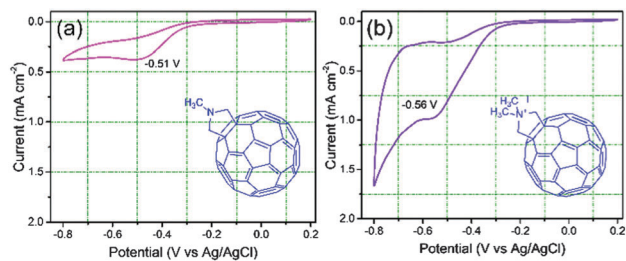


Fig. 3 Cyclic voltammetric curves of (a) MPC₆₀ and (b) quaternized N-methyl pyrrolidine-C₆₀ (QMPC₆₀) in O₂ saturated 0.1 M KOH.

(such as polymers of intrinsic microporosity,¹³ Troger base polymers¹⁴) could also possess such an ability for enhanced hydroxide conductivity (such a possibility is now being investigated).

Besides the highly conductive nature of the ionomer, the result of the ORR catalytic test was as astonishing as it was exciting. In investigating the effect of cationic head groups, model compounds with the same chemical structure were synthesized and investigated. Rotating disk electrode (RDE) tests were carried out on the newly synthesized MPC₆₀. Fig. 3a reproduces a typical cyclic voltammetric (CV) curve of MPC₆₀, showing an obvious cathodic peak at around -0.51 V in oxygen (O₂) saturated 0.1 M potassium hydroxide (KOH). Furthermore, the negative result of the methanol oxidation catalytic activity test of MPC₆₀ in 0.1 M KOH proves that the catalytic capacity of MPC₆₀ is exclusive (Fig. S3, ESI[†]), and that methanol is the fuel of the alkaline direct methanol fuel cell. To investigate whether pyrrolidinium cations still possess ORR catalytic capacity, MPC₆₀ was quaternized by methyl iodide in toluene (Fig. S4, ESI[†]). In other words, QMPC₆₀ was successfully synthesized and confirmed using NMR spectroscopy (Fig. S5, ESI[†]). The same RDE tests were performed for QMPC₆₀. Fig. 2b reproduces a typical CV curve of QMPC₆₀, showing a similar cathodic peak at around -0.56 V. This indicates that the fullerene derivative still possesses ORR catalytic capacity after quaternization. It is worth mentioning that the chemical structure of QMPC₆₀ remains the same as that of the designed pyrrolidinium based AEI shown in Fig. 1. The onset potentials of MPC₆₀ and QMPC₆₀ are the same, at around -0.2 V [*versus* silver/silver chloride (Ag/AgCl)], whereas QMPC₆₀ exhibits a higher current density. This is attributed to the increased conductive nature of QMPC₆₀ resulting from the quaternization. Compared with a commercial Pt/C catalyst, an inferior performance is observed (Fig. S6, ESI[†]). This suggests that further optimization/modification is critical for the fullerene derivatives to be utilized alone as an ORR catalyst. Unlike traditional cationic head groups, this research proves the positive effect of the C₆₀ base anion exchangeable head groups. This is considerable progress in the development of novel AEI.

Considering the highly hydroxide conductive nature and its ability to interfere with ORR, incorporating the as-prepared AEI into the fuel cell electrode assembly should greatly reduce the internal resistance. The papers by Noto *et al.* and Pandey *et al.* discuss the phase-separated nanostructure of a generic polymer electrolyte and can be referred to, to better understand the conduction mechanism for the as-prepared ionomer.^{16–18}

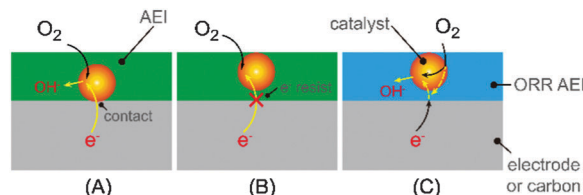


Fig. 4 Schematic illustration of the ionomer-catalyst interaction when they are in direct contact (A), surrounded by common AEI (B) and when AEI with ORR interference ability is employed (C).

As shown in Fig. 4, the catalyst nanoparticles are commonly bound together in the electrode by AEI, for example Nafion or Tokuyama AS-4.¹⁵ Conventionally, the electrons and hydroxide ions in ORR can be transferred smoothly when the catalysts are in direct contact with the electrode or the carbon support (Fig. 4A). However, when the catalyst is completely wrapped by the ionomers (Fig. 4B), the hydroxide generated in the ORR could be transferred *via* cationic head groups but the electron transfer pathway is blocked by polymeric ionomers. In contrast, the resistance should be decreased if the ionomers are involved in ORR even when catalysts are completely wrapped, which is exactly the case when as-prepared BPPO-MPC₆₀ is applied (Fig. 4C). By matching the electron transfer pathway with the hydroxide conductive pathway, the poisoning of the catalyst by conventional cationic head groups is avoided. It should be noted that, even though a metal catalyst, for example Pt/C, contributed mainly to the ORR, the impact of MPC₆₀ ORR activity on the overall performance of the AEMFC is expected to be minor regardless of the high ionic conductivity. A synergistic effect might exist between the fullerene cations and the catalyst leading to higher catalyst activity. Additional resistance still exists because of the presence of the polymeric backbone. However, it can be further reduced by incorporating conducting polymer backbones, such as poly(thiophene).¹⁹ As previously stated, it is easy to incorporate such a conductive polymer backbone.

The BPPO-MPC₆₀ ionomer also exhibits satisfactory mechanical properties and thermal properties, which result from the low ion exchange capacity and the special structure of the functional groups. The highest water uptake obtained at 80 °C is 3.65% (Table S1, ESI[†]), which is extremely low compared with typical AEIs. The swelling ratio of the ionomer is very tiny ($<2\%$) after immersion in water indicating high dimensional stability. Low water uptake and high dimensional stability can lower the risk of MEA delamination during fuel cell operation. Thermal stability analysis demonstrates that the pyrrolidinium cations degrade at around 300 °C in a nitrogen atmosphere (Fig. S7, ESI[†]). The fuel cell system commonly operates at 60–80 °C. Thus, the thermal stability of the as-prepared ionomer meets the basic requirements.

In conclusion, novel fullerene-based cationic head groups for fabricating AEIs have been found. The fullerene derivative obtained and the fullerene cationic head groups show ORR catalytic activity in high pH conditions, which can eliminate the poisoning of conventional cationic head groups on the ORR catalyst. A robust, highly hydroxide conductive AEI was

obtained by incorporating such fullerene-based cationic head groups. Extremely low water uptake benefits the fabrication of MEA, avoiding possible delamination in the fuel cell operation. The methodology to match electron transfer and hydroxide conduction can be imitated to improve the APEFC efficiency. Such AEIs hold great potential for producing high performance APEFCs.

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Notes and references

- 1 A. L. Ong, D. K. Whelligan, M. L. Fox and J. R. Varcoe, *Phys. Chem. Chem. Phys.*, 2013, **15**, 18992–19000.
- 2 A. L. Ong, K. K. Inglis, D. K. Whelligan, S. Murphy and J. R. Varcoe, *Phys. Chem. Chem. Phys.*, 2015, **17**, 12135–12145.
- 3 S. Gu, W. Sheng, R. Cai, S. M. Alia, S. Song, K. O. Jensen and Y. Yan, *Chem. Commun.*, 2013, **49**, 131–133.
- 4 K. Matsumoto, T. Fujigaya, H. Yanagi and N. Nakashima, *Adv. Funct. Mater.*, 2011, **21**, 1089–1094.
- 5 N. Martin, *Chem. Commun.*, 2006, 2093–2104.
- 6 F. Diederich and C. Thilgen, *Science*, 1996, **271**, 317.
- 7 M. Maggini, G. Scorrano and M. Prato, *J. Am. Chem. Soc.*, 1993, **115**, 9798–9799.
- 8 M. L. Disabb-Miller, Y. Zha, A. J. DeCarlo, M. Pawar, G. N. Tew and M. A. Hickner, *Macromolecules*, 2013, **46**, 9279–9287.
- 9 Y. Z. Zhuo, A. L. Lai, Q. G. Zhang, A. M. Zhu, M. L. Ye and Q. L. Liu, *J. Mater. Chem. A*, 2015, **3**, 18105–18114.
- 10 Z. Yang, J. Zhou, S. Wang, J. Hou, L. Wu and T. Xu, *J. Mater. Chem. A*, 2015, **3**, 15015–15019.
- 11 J. Pan, C. Chen, Y. Li, L. Wang, L. Tan, G. Li, X. Tang, L. Xiao, J. Lu and L. Zhuang, *Energy Environ. Sci.*, 2014, **7**, 354–360.
- 12 S. Gu, R. Cai, T. Luo, Z. Chen, M. Sun, Y. Liu, G. He and Y. Yan, *Angew. Chem., Int. Ed.*, 2009, **48**, 6499–6502.
- 13 N. B. McKeown and P. M. Budd, *Chem. Soc. Rev.*, 2006, **35**, 675–683.
- 14 M. Carta, R. Malpass-Evans, M. Croad, Y. Rogan, J. C. Jansen, P. Bernardo, F. Bazzarelli and N. B. McKeown, *Science*, 2013, **339**, 303–307.
- 15 A. J. Lemke, A. W. O'Toole, R. S. Phillips and E. T. Eisenbraun, *J. Power Sources*, 2014, **256**, 319–323.
- 16 V. D. Noto, T. A. Zawodzinski, A. M. Herring, G. A. Giffin, E. Negro and S. Lavina, *Int. J. Hydrogen Energy*, 2012, **37**, 6120–6131.
- 17 V. D. Noto, G. A. Giffin, K. Vezzu, G. Nawn, F. Bertasi, T. Tsai, A. M. Maes, S. Seifert, E. B. Coughlin and A. M. Herring, *Phys. Chem. Chem. Phys.*, 2015, **17**, 31125–31139.
- 18 T. P. Pandey, A. M. Maes, H. N. Sarode, B. D. Peters, S. Lavina, K. Vezzù, Y. Yang, S. D. Poynton, J. R. Varcoe, S. Seifert, M. W. Liberatore, V. D. Noto and A. M. Herring, *Phys. Chem. Chem. Phys.*, 2015, **17**, 4367–4378.
- 19 S. Miyanishi, T. Fukushima and T. Yamaguchi, *Macromolecules*, 2015, **48**, 2576–2584.