Electronic Supplementary Material (ESI) for RSC Advances

Cationic fluorinated polymer binders for microbial fuel cell cathodes

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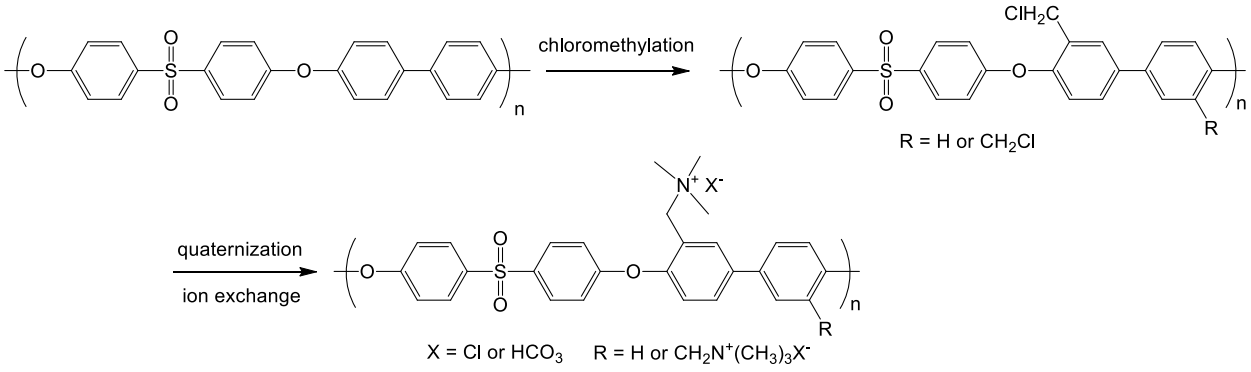
Supporting information

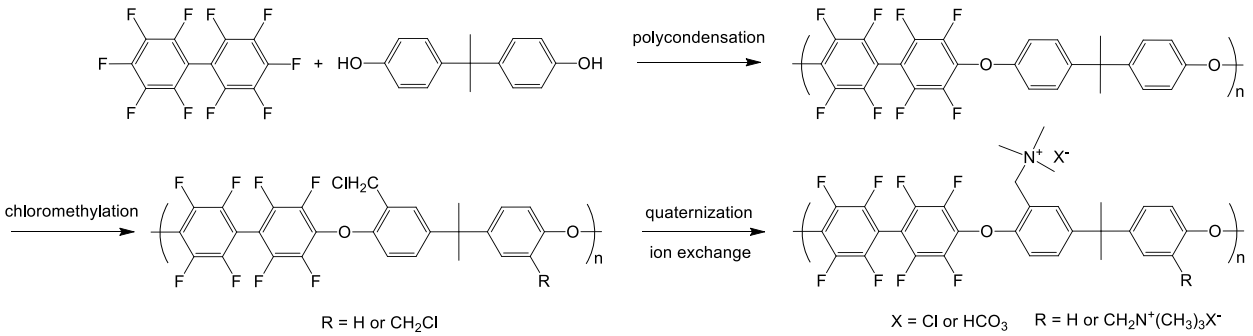
Synthesis of Q-Radel and Q-FPAEs

Q-Radel was synthesized via chloromethylation of Radel NT5500 (Solvay Advanced Polymers, Alphareta GA) and subsequent quaternization by trimethylamine according to standard procedures in the literature [1] (Scheme 1). Polymers were used in chloride counter ion form for making cathode binder solutions.

Fluorinated poly(arylene ether)s containing quaternary ammonium groups (Q-FPAEs) with different IECs were synthesized by two steps (Scheme 2). First, the backbone fluorinated poly (arylene ether) (FPAE) was synthesized via nucleophilic polycondensation of bisphenol A with decafluorobiphenyl [2]. The isolated and purified polymer was then chloromethylated and quaternized. The extent of chloromethylation was controlled by the duration of the chloromethylation reaction. The prepared series of fluorinated polymers were Q-FPAE-1.0-Cl, Q-FPAE-1.4-Cl and Q-FPAE-1.4-H, where the numbers and suffix denote the IEC and counter ions of polymers.



Scheme 1: Synthesis of Q-Radel.



Scheme 2: Synthesis of fluorinated polymers Q-FPAEs.

Preparation of polymer solutions

Solutions of the aromatic polymer binders explored in this work were made in an ethanol:water solvent mixture for cathode fabrication to mimic the commercially available NAFION® dispersions. Chloromethylated polymer powder was dissolved in chloroform to obtain a 5 % wt/vol polymer solution, which was then cast on a glass plate at room temperature. After being dried at 50 °C for 24 h under vacuum, the cast membrane was immersed into 45 wt% aqueous of trimethylamine solution for 48 h to quaternize the polymer. The quaternized anion exchange membrane (AEM) with bicarbonate counter ions was obtained by dipping the chloride form AEM into 1 M potassium bicarbonate solution for 48 h. Then, 1.0 g quaternary ammoniated membrane was added into 20 mL ethanol:water mixture solvent and stirred until most of membrane dissolved to form the ethanol:water polymer solution used for cathode fabrication. The S-Radel solutions were made by dissolving cast films from DMF solution in ethanol:water solution.

MFC performance

Figure S1 shows cell voltage of MFCs with different binders over the 19 cycle operation period studied in this work.

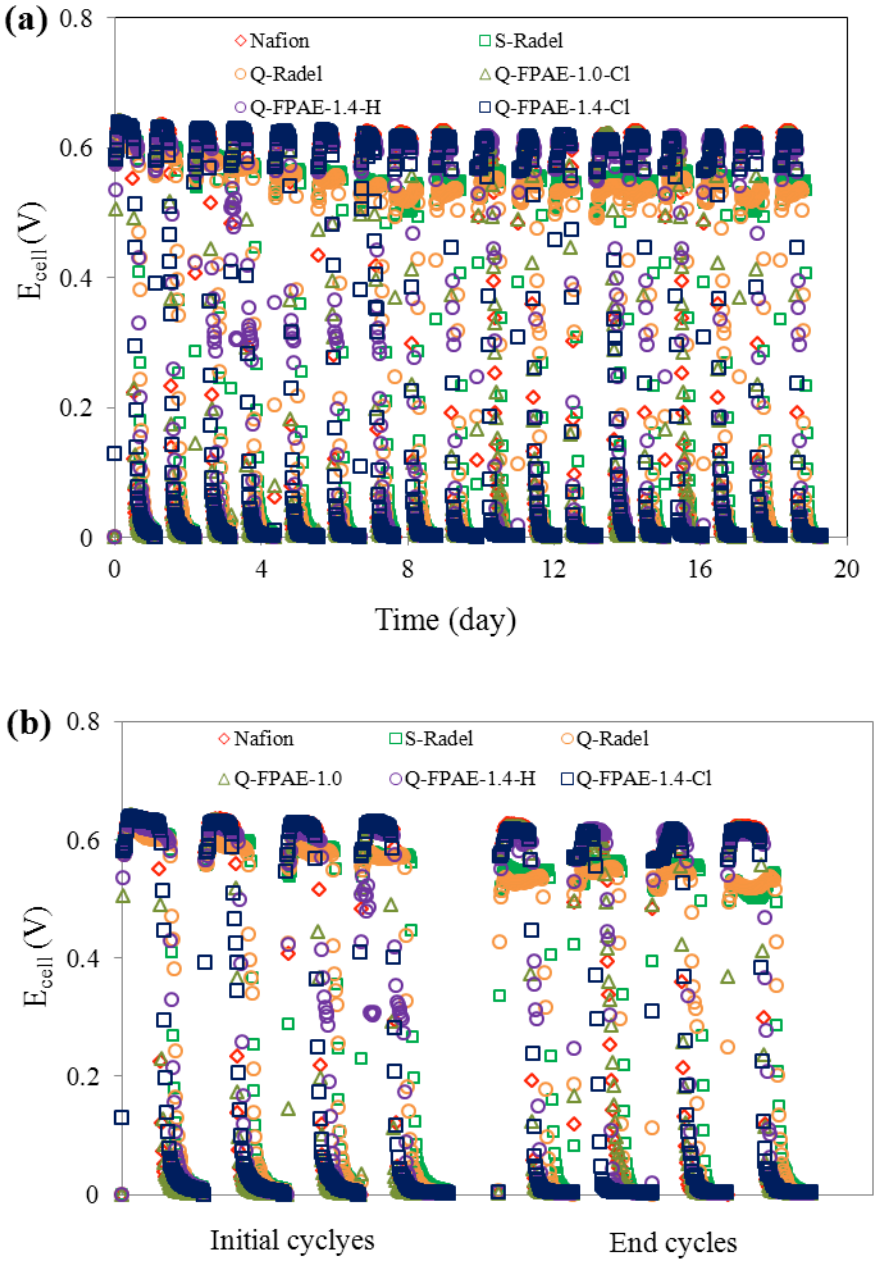


Figure S1: (a) Over whole operation period; (b) During initial 4 cycles and end 4 cycles.

Biofilm formation on cathodes with different polymer binders

Figure S2 shows an optical image of the cathodes after 19 MFC fed-batch cycles. The NAFION® and Q-FPAE samples showed significant biofilms on the surface of the cathode structure. The surface biofilms were not as evident on the S-Radel or Q-Radel samples that did not contain fluorine in the polymer structure.

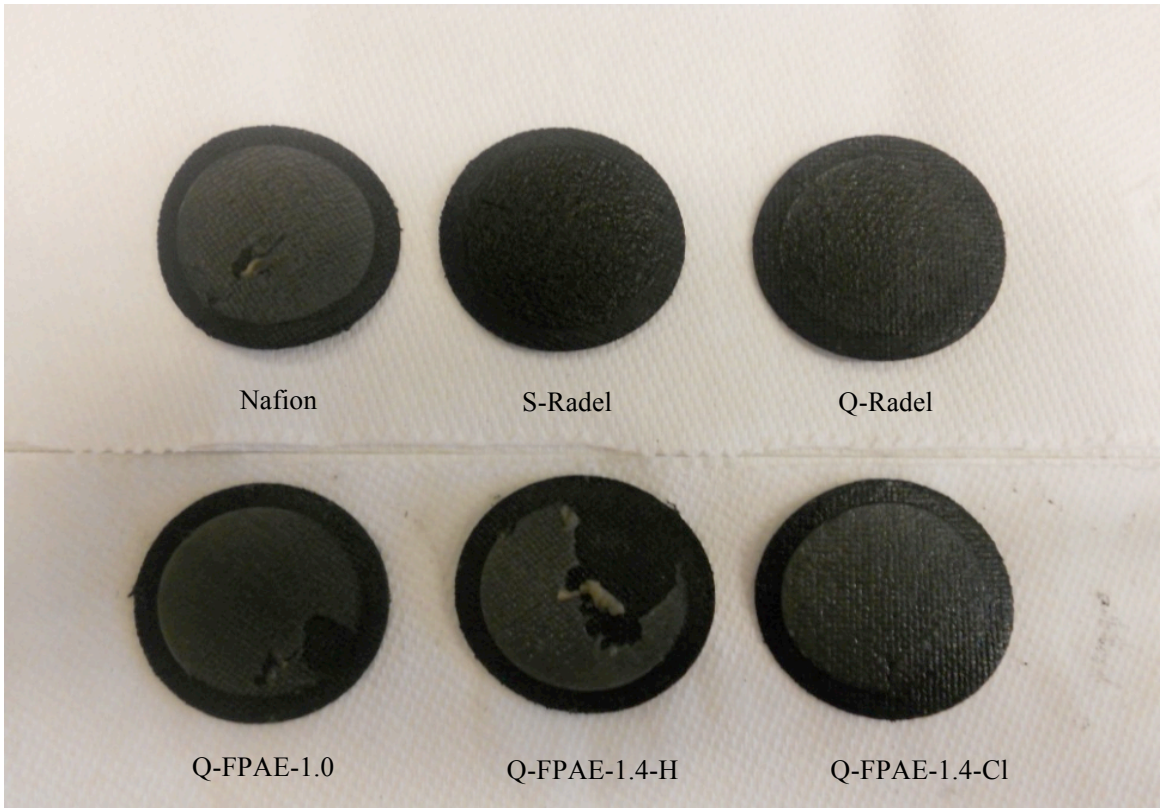


Figure S2: Optical images of biofilms on cathodes after 19 cycles. (From top left to right: Nafion, S-Radel, Q-Radel, Q-FPAE-1.0, Q-FPAE-1.4-H and Q-FPAE-1.4-Cl).

References

1 G. J. Hwanga, H. Ohya, Preparation of anion-exchange membrane based on block copolymers Part 1. Amination of the chloromethylated copolymers. *Journal of Membrane Science* 140 (1998) 195-203.

2 F. Merce, T. Goodma, J. Wojtowi, D. Duff, Synthesis and Characterization of Fluorinated Aryl Ethers Prepared from Decafluorobipheny. *Journal of Polymer Science: Part A Polymer Chemistry*, Vol. 30, 1767-1770 (1992).