# Relationships between Structure and Alkaline Stability of Imidazolium Cations for Fuel Cell Membrane Applications

Samuel C. Price,* Kristen S. Williams, and Frederick L. Beyer

Weapons & Materials Research Directorate, U.S. Army Research Laboratory, RDRL-WMM-G, Bldg 4600, Aberdeen Proving Ground, Maryland 21005, United States

S *Supporting Information*

ABSTRACT: Anion exchange membranes have substantial potential to be useful in methanol fuel cells due to the viability of non-noble metal electrocatalysts at high pH and increases in the oxidation rate of methanol in alkaline conditions. However, long-term stability of the cationic moiety has been an issue, and imidazoliums have recently attracted attention as candidates for stable cations. The prevailing strategy for increasing the stability of the imidazolium has involved adding sterically hindering groups at the 2 position. Surprisingly, the findings of this study show that steric hindrance is the least effective strategy for stabilizing imidazoliums. We propose that the most important stabilizing factor for an imidazolium is the ability to provide alternative, reversible deprotonation reactions with hydroxide and outline other structure–property relationships for imidazolium cations.
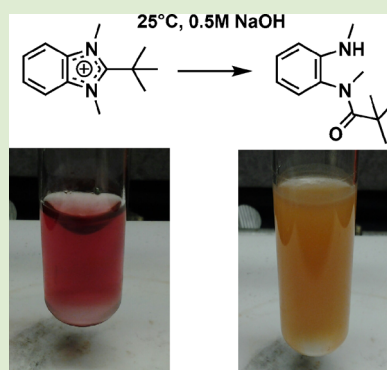
Anion exchange membranes (AEMs) have recently been a topic of research and development from academia and industry as a solution to problems with existing methanol fuel cell membranes. These include facile methanol oxidation kinetics at high pH and the ability to use non-noble catalysts in the fuel cell electrode assembly.[1−4] AEM performance is currently limited by low hydroxide conductivities, poor long-term (>5000 h) alkaline stability at 80 °C, poor mechanical properties, or a combination of these factors.[5]

The cationic group on the AEM responsible for transport of the hydroxide anion must be alkaline stable, while minimizing the amount of hydrophobic bulk around the cation so that high ion exchange capacities (IECs) of the final membrane may be accessed. Imidazolium cations have been the topic of extensive research by a number of research groups since they may possess alkaline stability at very low molar mass (111 g mol^{-1}) compared to phosphonium or sulfonium ions.[6−10] Table 1 summarizes the varying results reported in the recent literature for a variety of substituted imidazolium cations and the results reported in this work. Given the wide variety of testing conditions used and the wide range of stabilities reported, more rigorous and standardized test methodology is required for a clear analysis of stability to be possible.

Many groups have acknowledged this need for better test methodology. Hickner and co-workers have proposed degrading polymer materials in a 1.0 M potassium deuteroxide solution in 3:1 methanol:water at 80 °C.[11] This is an excellent method and should be widely adopted, but for our purposes it has a few minor drawbacks. Methanol is a poorer solvent for hydroxide anions and is known to cause faster degradation than the same experiments in water. Second, the polymer backbone may degrade faster than the ion, providing a competing use for

hydroxide in solution. Lastly, the polymer backbone weakens the NMR signal from the degrading cation and makes mechanistic determination of the cation degradation more difficult. Small molecule studies on the cation alone in hydroxide solution provide a simple test which can be completed before the corresponding polymer chemistry is optimized and are a good indicator of whether a cation will be stable when attached to the polymer backbone. Small molecule NMR degradation studies have been extensively used to determine the stability of benzyltrimethylammonium cations, the current commercially available choice for AEMs.[11−14]

Recently, the strategy of protecting the 2 position of the imidazolium from a hydroxide attack with additional steric bulk has become popular, with three research groups reporting improved stability of imidazoliums employing this steric bulk strategy.[16,18,19] Our interest in the stability of imidazolium ions originated from the synthesis of 2-*tert*-butyl-1,3-dimethyl-6-vinylbenzimidazolium salts (such as compound 6, Figure 1) for use as radical polymerization monomers that have the imidazolium stabilized by this steric hindrance strategy. In step 4 of the synthesis of compound 6, 2-*tert*-butyl-1-methylbenzimidazole (4) was produced as a side product of the formylation and was subsequently isolated and quaternized with iodomethane for preliminary base stability studies via NMR. Surprisingly, cation 5 exhibited exceptionally poor base stability, degrading completely to the corresponding benzamide 7 within one minute at room temperature in 0.5 M NaOH (Figure 2), prohibiting NMR studies. This remarkable

Table 1. Summary of the Alkaline Stabilities of Different Imidazolium Cations[a]

| Cation	Polymer Backbone	Test Conditions	Stability Test Method	Stability	Reference	Cation	Polymer Backbone	Test Conditions	Stability Test Method	Stability	Reference
	polysulfone	3M NaOH, 60°C, 24h	conductivity	Not Stable	11,12	**5**	none	0.5M NaOH, rt	NMR	$t_{1/2}$ = too fast to measure	This Work
	styrene	10M NaOH, 60°C, 120h	conductivity	Stable	13	**8**	none	1.0 M NaOH, 80°C	NMR	$t_{1/2}$ = 6400 minutes	This Work
	styrene & acrylonitrile	10M NaOH, 60°C, 72h	conductivity & IEC	Stable	14	**9**	none	1.0 M NaOH, 80°C	NMR	$t_{1/2}$ = 46 min	This Work
	PMMA	1 M NaOH, rt, 24h	NMR	Not Stable	15	**10**	none	1.0 M NaOH, 88°C	NMR	$t_{1/2} \geq 1000$ h	This Work
		2M KOH, 60°C, 13 days	IEC, NMR	Stable	16	**11**	none	1.0 M NaOH, 80°C	NMR	$t_{1/2}$ = 880 min	This Work
	PPhO	2M KOH, rt, 7 days	IEC, conductivity	Not Stable	17	**12**	None	1.0 M NaOH, 80°C	NMR	$t_{1/2}$ = 170 min	This Work
R' = H, Me	styrene & ETFE	1 M KOH, 60°C, 24h	conductivity, IEC, NMR	Not Stable	18	**13**	none	1.0 M NaOH, 80°C	NMR	$t_{1/2}$ = 779 min	This Work
R' = Me, iPr, Ph	none	1M KOH, 80°C, 168h	NMR	Stable	19	**14**	none	1.0 M NaOH, 88°C	NMR	$t_{1/2} \geq 1000$ h	This Work
	none	2M KOH in water, 80°C	NMR	$t_{1/2}$ = 45 h	8,20-23		none	1.0 M NaOH, 80°C	NMR	$t_{1/2} \geq 400$ h	This Work

[a]R groups represent the polymer backbone unless otherwise noted.
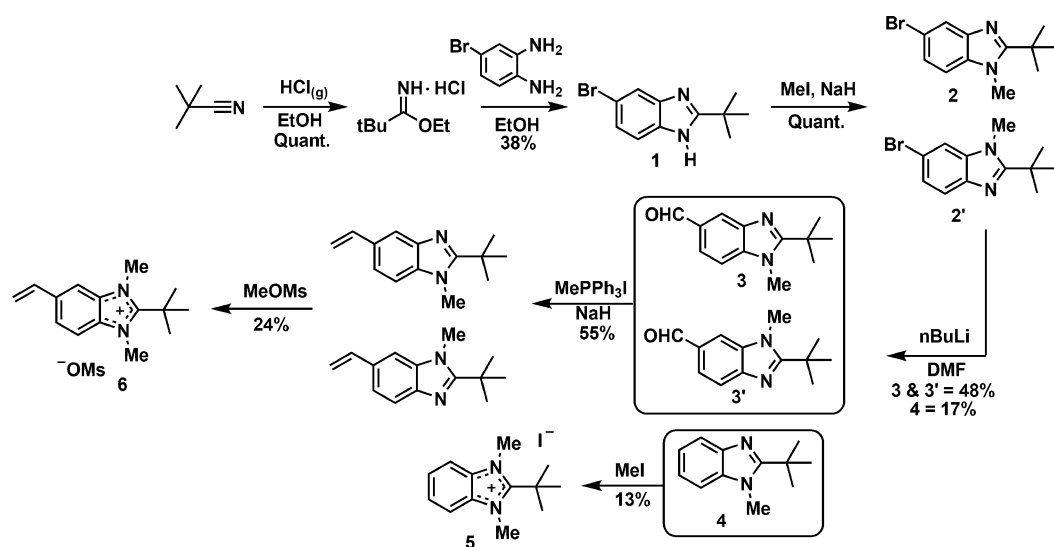
Figure 1. Synthesis of cations 5 and 6. Cation 5 could be synthesized more directly, but it was more efficient to isolate as a byproduct of the formylation step.
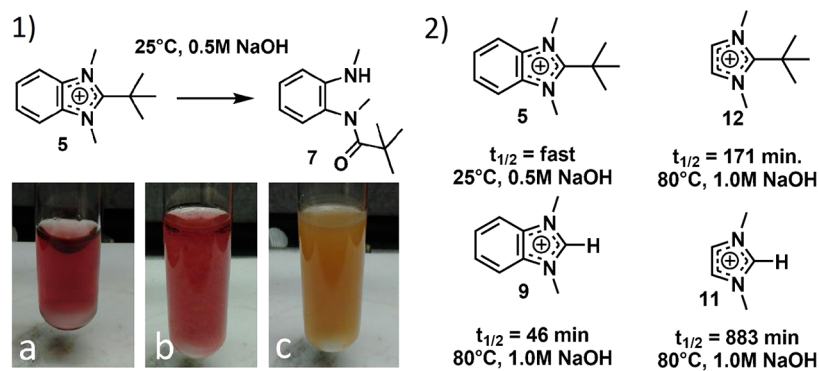
Figure 2. (1) Degradation of cation 5 in 0.5 M NaOH at room temperature. (a) Cation 5 dissolved in 3.5 mL of water. (b) 30 s after 3.5 mL of 1 M NaOH was added, resulting in a cloudy precipitate forming. (c) 4 h after NaOH addition, noticeable color change. (2) Comparison of acidic imidazolium cations (9 and 11), with similar, more sterically hindered, and less acidic cations (5 and 12). In each case the more acidic cation degrades significantly slower.
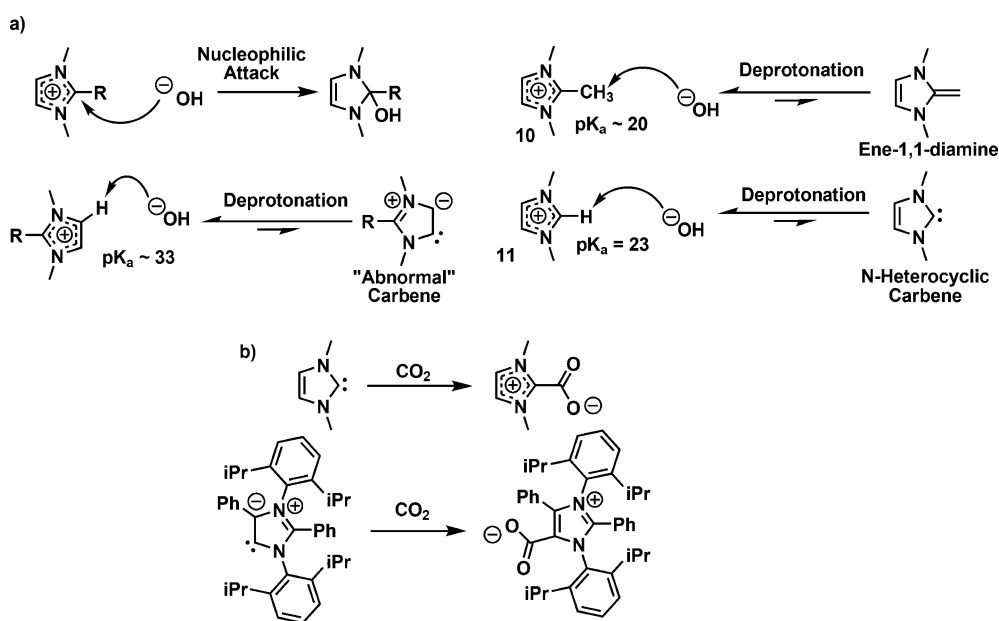

Figure 3. (a) Possible reactions of imidazolium cations in hydroxide solution. The three deprotonation reactions are reversible and quite rapid. Nucleophilic attack is the primary degradation mechanism. (b) Two examples of reported reactivity of deprotonated imidazolium intermediates with CO_2 from refs 23 and 24.

instability despite the sterically demanding *tert*-butyl group led us to further investigate the structure−property relationships for alkaline stability of imidazolium cations.

1,3-Dimethylbenzimidazolium iodide (9), the analogue of 5 without the *tert*-butyl group at the 2 position, displayed more alkaline stability than compound 5 despite going against conventional wisdom that more bulky substituents on the 2 position of the imidazolium should increase the base stability. When encountering a hydroxide ion in solution, for imidazolium cations with acidic protons, it is more rapid for the hydroxide to deprotonate the imidazolium than to attack the carbon at the 2 position. This is clear by NMR since it is well-known that all of the aromatic hydrogens and the protons from the methyl group are exchanged with deuterium within minutes at 80 °C (Figure S1 in the Supporting Information). Therefore, ions with acidic protons in proximity to the 2 carbon show slower degradation than ions without, all other factors being equal. This acidic proton stabilization is explicitly seen in Figure 2-2. Despite compound 5 having significantly more steric bulk at the 2 position, compound 9 is significantly more

stable. This acidic proton stabilization can also be seen in the work of Yan and co-workers, where 1,2,3-trimethylimidazolium (10) is stable in 2 M KOH at 80 °C but the phenyl-substituted analogue (8) degrades in the same conditions.[19] This result is confirmed in our work, with the 2-methyl-substituted imidazole showing an order of magnitude greater stability. Despite the increased size of the phenyl ring and the ability to stabilize the cation through resonance, the methyl group at the 2 position confers more stability. Clearly competing deprotonation reactions have a larger effect than steric or electronic factors when determining the reactivity of imidazolium derivatives to base.

While it is obvious from these results that incorporation of acidic protons on the imidazolium cation results in higher stability toward nucleophilic attack of hydroxide, it is not clear that this strategy will produce a membrane with long-term stability under the harsh conditions of a fuel cell. Both conventional and abnormal carbenes from deprotonated imidazoliums are known to be able to react with electrophiles such as CO_2 (Figure 3), which is present in methanol fuel cells
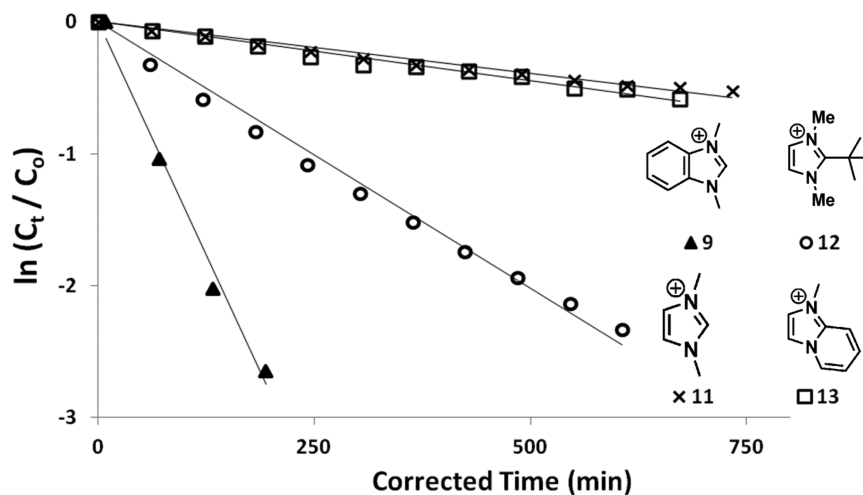
Figure 4. Degradation behavior of compounds 9 (filled triangles), 11 (✕'s), 12 (open squares), and 13 (open circles) dissolved in 1.0 M NaOD at 80 °C. Lines are linear fits of the data to a pseudo-first-order rate equation.
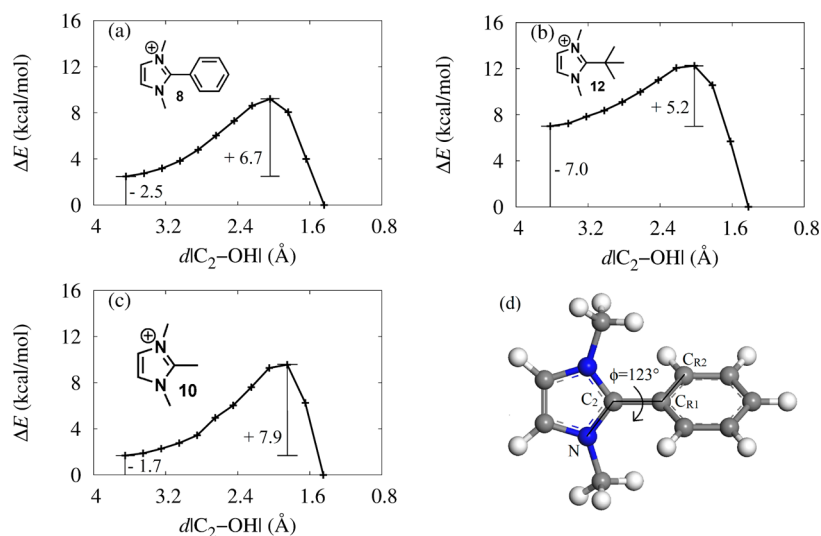
Figure 5. DFT-calculated relative energies (in kcal/mol) for intermediate configurations along the minimum energy path (MEP) of C_2-OH bond formation in (a) phenyl, (b) *tert*-butyl, and (c) methyl imidazolium derivatives. All energies are relative to the ground state structure in which a single OH moeity is bound at the 2 position. (d) DFT-calculated optimized geometry for compound 8.

from electro-oxidation.[24,25] So while these ions show stability in simple solution tests with no other compounds other than hydroxide and water to react with, the nucleophilic and reactive deprotonated species they form may reduce their long-term (>5000 h) stability within a fuel cell membrane and should be of concern to membrane developers.

A comparison of the stability behavior between compounds 9 and 5 and compounds 11 and 12 clearly shows that competing deprotonation reactions at the 2 position are more effective at stabilizing the imidazolium cation than introucing steric hindrance. Fusing a benzene ring to the 1 and 2 positions of the imidazole ring (compound 13) provides electron resonance stabilization, which is similarly effective at retarding degradation as providing an acidic site on the imidazolium, since compounds 11 and 13 degrade at almost the same rate. The first-order half-lives of compounds 9, 11, 12, and 13 are 46, 883, 171, and 779 min, respectively, at 80 °C in 1 M NaOD, shown in Figure 4. Compared to the standard benzyltrimethylammonium cation half-life of 2700 min at 80 °C in 2 M KOH, these imidazoliums fall far short of improving alkaline stability.

To further investigate the thermodynamic stability of different imidazolium derivatives in alkaline environments, we calculated the minimum energy path (MEP) for reaction of an isolated hydroxide group with the 2 atom in the imidazolium. To map the MEP, we perform a scan of the C_2-OH bond distance, allowing all other coordinates to relax. We scan the C_2-OH bond distance in 0.2 Å increments from 3.6 Å to the C–O bond length of roughly 1.4 Å. The resulting MEPs for compounds 8, 10, and 12 are shown in Figure 5(a–c). From these, we can obtain the free energies of reaction and activation barriers for hydroxide attack at the 2 position. For all compounds, we find that the addition of hydroxide at the 2 position is an exothermic reaction, and compound 12—the *tert*-butyl derivative—has the largest free energy of reaction of −7.0 kcal/mol. Reaction energies for the phenyl and methyl derivative are smaller at −2.5 and −1.7 kcal/mol, respectively. Hence, the *tert*-butyl derivative has the largest thermodynamic driving force for attack at the 2 position. Furthermore, the activation barrier for formation of the C_2-OH bond in the *tert*-butyl derivative is the smallest at +5.2 kcal/mol. Activation

barriers for the phenyl and methyl derivatives are slightly larger at +6.7 and +7.9 kcal/mol, respectively. When comparing all three imidazolium compounds, we found that the slightly lower activation barrier and much larger reaction energy for hydroxide attack of the *tert*-butyl derivative are consistent with the enhanced degradation of this compound in alkaline environments. The high reaction energy may originate from 1,3-allylic strain between the *N*-methyl hydrogens and the protons on the *tert*-butyl group.[26] The methyl and phenyl derivatives have similar reaction barriers and energies, yet the methyl derivative (10) shows significantly enhanced stability compared to compound 8. The stability of compound 10 in alkaline environments may be enhanced by deprotonation side reactions, but such reactions are not considered in the MEP scans shown in Figure 5.

Finally, aliphatic ammonium cation 14 and 1,2,3-trimethyli-midazolium iodide (10) were examined for stability in basic conditions. Cation 14 was selected as a nonbenzylic ammonium cation that shows stability in the theoretical literature, and it possesses a functional handle in the alcohol group which can be used to attach it to a polymer backbone.[27] Both materials are stable past 16 h at 80 °C and show no traces of any degradation products forming during that time. Therefore, the materials were allowed to degrade in 1 M NaOD at 88 °C for 167 h, using ethylene glycol as an internal standard since dioxane showed signs of evaporation at this elevated time and temperature despite being sealed in a polyethylene centrifuge tube. After this time period, a white precipitate had formed in each sample, and this precipitate was insoluble in chloroform and water. Upon inspection by ^{1}H NMR, 82% of the imidazolium 10 and 95% of aliphatic cation 14 were remaining when compared to the ethylene glycol internal standard (Figure S2 and Figure S3 in the Supporting Information). These values are near the limit of detection for the experiment but are sufficient to roughly approximate a pseudo-first-order half-life greater than 1000 h for the 1,2,3-trimethylimidazolium (10) and cation 14, which make them candidates for further study within a fuel cell membrane.

To summarize, the stabilization of imidazolium cations is a complex relationship between sterics, electronics, and compet-ing reactions. The significant stability of compound 10 (1,2,3-trimethylimidazolium) is caused by the acidity of the methyl protons at the 2 position. The additional steric hindrance added by the methyl group likely slows the reaction by a negligable amount. In order of effectiveness, the following are the available ways to increase alkaline stability of imidazolium cations: (1) competing deprotonations, (2) electronic stabilization of the 2 carbon through resonance such as other aromatic substituents, and (3) steric stabilization about the 2 carbon. 1,2,3-Trimethylimidiazolium cations show good stability in alkaline solution due to the competing deprotonation reaction; however, stability in fuel cell conditions, particularly in the presence of CO_2, should still be investigated. Finally, aliphatic ammonium cations such as compound 14 show similar stability and should also be given increased attention from the AEM design community.

■ EXPERIMENTAL SECTION

Representative 16 h Degradation Experiment. 1,3-Dimethy-limidazolium iodide (11 mg, 0.049 mmol, 0.1 M) was dissolved into 0.5 mL of 1.0 M NaOD, 0.0636 M dioxane, or ethylene glycol solution in D_2O. The mixture was then added to an NMR tube, and within 15 min a proton NMR spectrum was collected at room temperature. The

sample was then heated to 80 °C, and the time at which the sample reached 77 °C was recorded. Proton NMR spectra were then collected while maintaining 80 °C for 14−16 h. The sample was then cooled to room temperature, and a final proton spectrum was collected. The first point collected at 80 °C while the sample was still equilibrating to temperature was omitted when fitting the points to a pseudo-first-order rate law, and the second point is used as time zero. The natural log of the percent of the cation remaining is then plotted vs this corrected time and fit to a pseudo-first-order rate equation. Very stable cations will not degrade under these conditions, likely because the glass NMR tube provides a competing use for hydroxide ions, and the short reaction times are not sufficient to cause degradation.

Representative 167 h Degradation Experiment. 1,2,3-Trimethylimidazolium iodide (24 mg, 0.1 mmol, 0.1 M) was dissolved into 1.0 mL of 1.0 M NaOD and 0.0636 M ethylene glycol solution in D_2O. A proton NMR spectrum was collected, and the mixture was then added to a 1.5 mL polyethylene centrifuge tube. The tube was sealed and placed in an oven at 88 °C. After 167 h, the sample was removed, the solvent decanted from the precipitate, and a final NMR spectrum collected.

■ ASSOCIATED CONTENT

ⓢ Supporting Information
Synthesis methodology, NMR spectra, and other detailed experimental information. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: samuel.c.price7.ctr@mail.mil.

Author Contributions
The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

■ REFERENCES

(1) Varcoe, J. R.; Slade, R. C. T. *Fuel Cells* **2005**, *5*, 187−200.
(2) Lu, S.; Pan, J.; Huang, A.; Zhuang, L.; Lu, J. *Proc. Natl. Acad. Sci.* **2008**, *105*, 20611−20614.
(3) Spendelow, J. S.; Wieckowski, A. *Phys. Chem. Chem. Phys.* **2007**, *9*, 2654−2675.
(4) Tripkovic, A. V.; Popovic, K. D.; Grgur, B. N.; Blizanac, B.; Ross, P. N.; Markovic, N. M. *Electrochim. Acta* **2002**, *47*, 3707−3714.
(5) Pivovar, B. In http://www.osti.gov/bridge/servlets/purl/1036037/; National Renewable Energy Laboratory, 2012 (Accessed 1/10/2014).
(6) Gu, S.; Cai, R.; Luo, T.; Chen, Z.; Sun, M.; Liu, Y.; He, G.; Yan, Y. *Angew. Chem., Int. Ed.* **2009**, *48*, 6499−6502.
(7) Gu, S.; Cai, R.; Yan, Y. *Chem. Commun.* **2011**, *47*, 2856−2858.
(8) Noonan, K. J. T.; Hugar, K. M.; Kostalik, H. A.; Lobkovsky, E. B.; Abruña, H. c. D.; Coates, G. W. *J. Am. Chem. Soc.* **2012**, *134*, 18161−18164.
(9) Zhang, B.; Gu, S.; Wang, J.; Liu, Y.; Herring, A. M.; Yan, Y. *RSC Adv.* **2012**, *2*, 12683−12685.
(10) Zha, Y.; Disabb-Miller, M. L.; Johnson, Z. D.; Hickner, M. A.; Tew, G. N. *J. Am. Chem. Soc.* **2012**, *134*, 4493−4496.

(11) Zhang, F.; Zhang, H.; Qu, C. *J. Mater. Chem.* **2011**, *21*, 12744−12752.

(12) Chen, D.; Hickner, M. A. *ACS Appl. Mater. Interfaces* **2012**, *4*, 5775−5781.

(13) Li, W.; Fang, J.; Lv, M.; Chen, C.; Chi, X.; Yang, Y.; Zhang, Y. *J. Mater. Chem.* **2011**, *21*, 11340−11346.

(14) Lin, B.; Qiu, L.; Lu, J.; Yan, F. *Chem. Mater.* **2010**, *22*, 6718−6725.

(15) Ye, Y.; Elabd, Y. A. *Macromolecules* **2011**, *44*, 8494−8503.

(16) Thomas, O. D.; Soo, K. J. W. Y.; Peckham, T. J.; Kulkarni, M. P.; Holdcroft, S. *J. Am. Chem. Soc.* **2012**, *134*, 10753−10756.

(17) Lin, X.; Liang, X.; Poynton, S. D.; Varcoe, J. R.; Ong, A. L.; Ran, J.; Li, Y.; Li, Q.; Xu, T. *J. Membr. Sci.* **2013**, *443*, 193−200.

(18) Page, O. M. M.; Poynton, S. D.; Murphy, S.; Lien Ong, A.; Hillman, D. M.; Hancock, C. A.; Hale, M. G.; Apperley, D. C.; Varcoe, J. R. *RSC Adv.* **2013**, *3*, 579−587.

(19) Lin, B.; Dong, H.; Li, Y.; Si, Z.; Gu, F.; Yan, F. *Chem. Mater.* **2013**, *25*, 1858−1867.

(20) Nuñez, S. A.; Hickner, M. A. *ACS Macro Lett.* **2012**, *2*, 49−52.

(21) Einsla, B. R.; Chempath, S.; Pratt, L.; Boncella, J.; Rau, J.; Macomber, C.; Pivovar, B. *ECS Trans.* **2007**, *11*, 1173−1180.

(22) Deavin, O. I.; Murphy, S.; Ong, A. L.; Poynton, S. D.; Zeng, R.; Herman, H.; Varcoe, J. R. *Energy Environ. Sci.* **2012**, *5*, 8584−8597.

(23) Bauer, B.; Strathmann, H.; Effenberger, F. *Desalination* **1990**, *79*, 125−144.

(24) Tommasi, I.; Sorrentino, F. *Tetrahedron Lett.* **2006**, *47*, 6453−6456.

(25) Aldeco-Perez, E.; Rosenthal, A. J.; Donnadieu, B.; Parameswaran, P.; Frenking, G.; Bertrand, G. *Science* **2009**, *326*, 556−559.

(26) Hoffmann, R. W. *Chem. Rev.* **1989**, *89*, 1841−1860.

(27) Long, H.; Kim, K.; Pivovar, B. S. *J. Phys. Chem. C* **2012**, *116*, 9419−9426.