Influence of ammonium– and imidazolium– cationic species on the oxygen reduction reaction on polycrystalline platinum disk electrodes in CO_2–contaminated alkaline media

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ABSTRACT

The onset of anthropogenic climate change, via carbon dioxide (CO_2) emissions and rapidly increasing global energy demand, is the driver for the development of clean renewable energy sources and carbon dioxide utilization (CDU). These has been a rapid development of the use of alkaline anion-exchange membrane (AAEM) in fuel cells due to many perceived advantages: tolerant to CO_2–derived precipitates, the use of cheaper electrocatalysts and improved cathode electrokinetics (*1*), minimized fuel cross–over, and novel water management possibilities.

AAEM–containing fuel cells operating in carbonate anion cycle is a prospective new and renewable power and CDU system (*2*, *3*). To accomplish this, researchers are actively investigating carbonate-selective electrocatalysts (*4*), carbonate–conductive AAEMs (*1-3*, *5*, *6*) and the effect of CO_2 on the performance of solid alkaline fuel cells (*7-9*). The development of imidazolium– and quaternary ammonium– functionalized AAEMs has recently incurred debates in term of high pH stability (*10*, *11*). However, the interaction between traces of such cationic species and the electrocatalysts in CO_2–exposed or CO_3^{2-}–containing alkaline electrolytes has not been comprehensively studied to date. Such information is particularly important in the development of AAEM–containing carbonate–cycle fuel cells.

In this work, cationic benzyltrimethylammonium (BTMA) and 1–benzyl–3–methylimidazolium (BMI) have been selected as the model molecules (Scheme 1). The influence of the 1 mM concentrations of these species on the oxygen reduction reaction (ORR) on polycrystalline platinum disk electrodes (Pt_{pc}) has been electrochemically studied in KOH (1 M) alkaline electrolytes, containing different concentrations of potassium carbonate (K_2CO_3). Cyclic and hydrodynamic linear sweep voltammetry techniques will be reported. The dramatic changes in the linear sweep voltammograms in Fig. 1 strongly suggest that both the BTMA and BMI cations significantly interact with the Pt_{pc} surface in strong alkaline electrolytes and decreased the ORR activity. The ORR activity on Pt_{pc} is particularly sensitive to CO_3^{2-} concentrations in the presence of BMI, especially at higher concentrations (≥ 50 mM K_2CO_3), whilst the activities were less dependent on CO_3^{2-} concentrations in the presence of BTMA.

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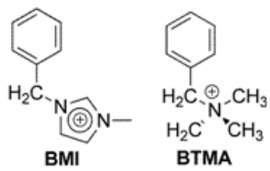
REFERENCES

1. J. R. Varcoe *et al.*, *Chemistry of Materials* **19**, 2686 (2007).
2. M. Unlu, J. Zhou, P. A. Kohl, *Electrochemical and Solid State Letters* **12**, B27 (2009).
3. C. M. Lang, K. Kim, P. A. Kohl, *Electrochemical and Solid State Letters* **9**, A545 (2006).
4. J. A. Vega, N. Spinner, M. Catanese, W. E. Mustain, *Journal of The Electrochemical Society* **159**, B19 (2012).
5. H. A. Kostalik *et al.*, *Macromolecules* **43**, 7147 (2010).
6. Y. Ye, Y. A. Elabd, *Macromolecules* **44**, 8494 (2011).
7. J. A. Vega, W. E. Mustain, *Electrochimica Acta* **55**, 1638 (2010).
8. K. N. Grew, X. Ren, D. Chu, *Electrochemical and Solid State Letters* **14**, B127 (2011).
9. M. Inaba *et al.*, *Electrochemistry* **79**, 322 (2011).
10. O. I. Deavin *et al.*, *Energy and Environmental Science* **5**, 8584 (2012).
11. B. Qiu, B. Lin, L. Qiu, F. Yan, *Journal of Materials Chemistry* **22**, 1040 (2012).



Scheme 1. The molecular structures of the investigated cationic head–group mimic molecules: Imidazolium (BMI) and quaternary ammonium (BTMA).

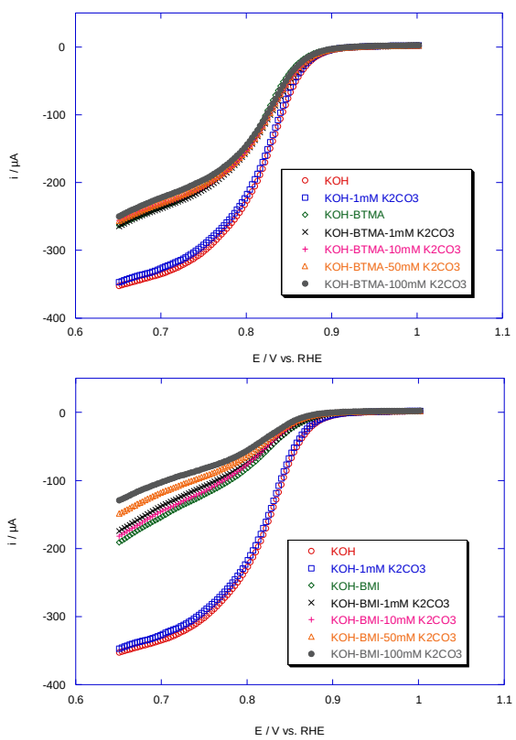


Fig. 1. The linear sweep voltammograms of ORR on Pt_{pc} electrode in O_2-saturated aqueous KOH (1 M) with and without added carbonate and head-group cationic species. Test at 5 mV · s^{-1}, 1600 rpm and 25 °C.