

## Blended Polyphosphazene Membranes for Direct Methanol Oxidation: Methanol Crossover and Steady State DMFC Measurements in Single Cells

S. Mukerjee<sup>1</sup>, R. C. Urian<sup>1</sup>, V. Shah<sup>1</sup>, P. N. Pintauro<sup>2</sup> and C. Byrne<sup>3</sup>

Department of Chemistry, 1 Hurtig Hall  
Northeastern University, 360 Huntington Avenue  
Boston, MA 02115

Department of Chemical Engineering  
Tulane University, New Orleans, LA 70118

Science Research Laboratory  
15 Ward Street, Somerville, MA, 02143

Polyphosphazenes are an interesting class of polymers because they combine the attributes of a low  $T_g$  polymer (high degree of polymer chain flexibility) with high temperature polymer stability<sup>1, 2</sup>. From a synthetic perspective, polyphosphazene constitutes one of the most mature inorganic-backbone polymer systems. With appropriate functionalization of the basic poly(dichlorophosphazene) backbone an unlimited number of specialty polymers can be synthesized. These unlike hydrocarbon polymers are generally resistant to chemical and thermal degradation<sup>2</sup>. Although polyphosphazenes have been explored for their use as solvent free solid polymer electrolytes in lithium batteries<sup>3</sup> its use as alternative membranes in PEM fuel cells both for reformat based systems and direct methanol is just emerging. Its application in direct methanol fuel cells is particularly significant based on the wide range of possible microstructures with differing proton conductivity and methanol crossover. This is based on the unique capability of adding different side chains to the polymer's P-N backbone that can be sulfonated.

Methanol crossover is one of the most important impediments in the viability of DMFC's. Central to this issue is the unacceptably high crossover of methanol in Nafion<sup>®</sup> type membranes. In Nafion<sup>®</sup>, the water and methanol sorption cannot be controlled independently of the membrane's ion exchange capacity because the polymer is not crosslinked and the swelling is dependent on both the membranes ion exchange capacity as well as polymers crystallinity. Water diffuses through Nafion due to the inherent hydrophobicity of the polymer's PTFE backbone and the side chains, resulting in the absence of strongly hydrated/hydrogen bonded water in the membrane<sup>4</sup>. Prior work by Prof. Pintauro<sup>5, 6</sup> has shown that well equilibrated crosslinked membranes based on poly[bis(3-mthylphenoxy)phosphazene] (with 15wt/o benzophenone) possessed an ion exchange capacity of 1.4 mmol/g and a high proton conductivity (~0.07 S/cm).

This presentation will focus on the methanol crossover measurements in a DMFC single cell at the fuel cell operating temperatures (in the range 40-70°C). Comparison will be made with current state of the art Nafion<sup>®</sup> membranes as a function of methanol concentration (in the range 1-10M). In addition, steady state polarization measurements will be presented in a DMFC in the same fuel cell operating conditions as mentioned above. To our knowledge these measurements constitute the first of their kind for a sulfonated/crosslinked polyphosphazene membrane.

### Experimental

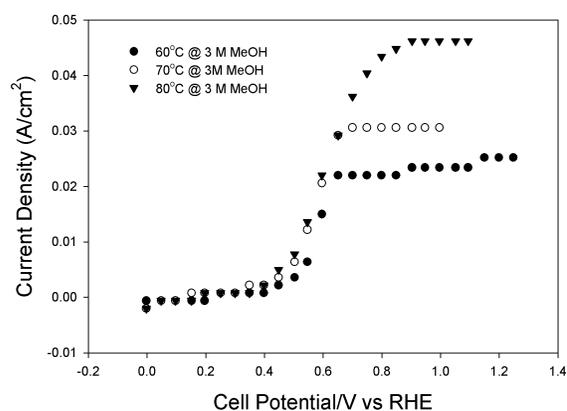
Methodology used for the preparation of the

membrane is described in a separate joint abstract with Tulane University, Carter *et al.*, submitted to the same symposium. These polymers prepared by sulfonating poly[bis(3-methylphenoxy)phosphazene] (700,000 MW) were blended with known amounts of PVDF (polyvinylidene fluoride), known by its trade name as Kynar [Attofina, USA]. Both Kynar 761 and Kynar-Flex were used. The films were cast into films, which were typically 100 $\mu$ m thick. These films were subsequently radiation crosslinked with electron beam at Science Research Laboratory (MA). Various dose levels were used for this purpose.

Fuel cell tests and cross over measurements were conducted in a specially constructed DMFC, which had an in built dynamic reference electrode, thus allowing for simultaneous anodic half-cell polarization measurements. In addition, there were the usual arrangements of controlling the cell temperature, preheating the methanol stream as well as controlling the flow rate (peristaltic pump). Methodology for methanol crossover measurements followed those described earlier for Nafion membranes<sup>7</sup>.

### Results

Figure 1 shows limiting current behavior in a DMFC single cell using the procedure outlined elsewhere<sup>7</sup>. The comparison shows an approximately one order of magnitude lower crossover for blended polyphosphazene membrane as compared to Nafion 117.



This presentation will focus on the impact of these measurements as well as single and half-cell polarization measurements as a function of methanol concentration in the range of (1 to 10 M).

### Acknowledgements

The authors wish to acknowledge, the Army Research Office for sponsoring this work under the auspices of an STTR program funded at Science Research Laboratories with Tulane and Northeastern Universities serving as subcontractors.

### References

- <sup>1</sup> P. Potin, and R. Dejaeger, *Eur. Polym. J.*, **27**, 341 (1991).
- <sup>2</sup> H. R. Allcock, R. J. Fitzpatrick, L. Salvati, *Chem. Mater.*, **3**, 1120 (1990).
- <sup>3</sup> P. M. Blonsky, D. F. Shriver, P. Austin, and H. R. Allcock, *Macromolecules*, **21**, 2299 (1988).
- <sup>4</sup> M. Falk., *ACS Symposium Series No. 180*, ACS, Washington D. C. p 137 (1980).
- <sup>5</sup> Q. Guo, P. N. Pintauro, H. Tang, S. O'Conner., *J. Mem. Sci.*, **154**, 175 (1999).
- <sup>6</sup> H. Tang, and P. N. Pintauro, *J. Appl. Polym. Sci.*, **79**, 49 (2000).
- <sup>7</sup> X. Ren, T. E. Springer, and T. Zawodzinski, *J. Electrochem. Soc.*, **147**, 466 (2000).