

Conductive Polymers as Positive Electrodes  
in Rechargeable Aluminum Batteries

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Rechargeable batteries based on aluminum are attractive alternatives to those based on conventional chemistries because of the low cost and high charge-storage capacity of aluminum. Aluminum is the most abundant metal in the earth's crust, and its cost is significantly lower than that of most other metals used for electrochemical energy storage. The volumetric capacity of aluminum metal is  $8.0 \text{ Ah cm}^{-3}$ , which is four times higher than that of lithium. Aluminum is also competitive in terms of gravimetric capacity ( $3.0 \text{ Ah g}^{-1}$  vs. lithium's  $3.9 \text{ Ah g}^{-1}$  or sodium's  $1.2 \text{ Ah g}^{-1}$ ). Aluminum batteries based on aqueous or high-temperature molten salt electrolytes have been the subject of extensive research but have faced prohibitive technical barriers (1). An alternative type of rechargeable aluminum battery is based on room-temperature ionic liquids containing imidazolium salts and aluminum chloride (2). Electrochemical plating and stripping of aluminum metal in such solutions have been studied in detail (3-5), forming the basis for the negative electrode in a rechargeable aluminum battery. Active materials for the positive electrode have been far less explored.

Presented here is the use of conductive polymers as anion-insertion electrodes in rechargeable aluminum batteries operating at room temperature. Such polymers can be electrochemically oxidized and reduced in chloroaluminum ionic liquids at room temperature. Concurrent with electro-oxidation, the polymer is doped with anions from the solution to maintain electro-neutrality. Upon electro-reduction of the polymer, the anions are transferred back to solution. Such cycling has been demonstrated with polypyrrole (6), polythiophene (7), and polyaniline (8), but metrics that are important for battery characterization (such as specific capacity, coulombic efficiency, and cycling stability) were not reported in detail.

Conjugated monomers, such as pyrrole and thiophene, were electrochemically polymerized at room temperature on glassy carbon electrodes in neutral (1:1 molar) mixtures of  $\text{AlCl}_3$  and 1-ethyl-3-methylimidazolium chloride (EMIC). Electrochemical testing of the polymer films was then performed in acidic mixtures of  $\text{AlCl}_3$  and EMIC, in which aluminum metal can be reversibly stripped and plated at the counter electrode. This is distinct from previous reports that examined electrochemical activity only in neutral or basic solutions (6, 7).

As shown by the CV in Figure 1, electropolymerized polypyrrole in the ionic liquid exhibited faradaic activity (a single redox peak-pair) at low potential ( $0.36 \text{ V vs. Al/Al}^{3+}$ ) and non-faradaic activity over the full potential range tested. In contrast, the polythiophene film exhibited a redox peak-pair at higher potential ( $1.2 \text{ V vs. Al/Al}^{3+}$ ). Galvanostatic cycling of polythiophene in acidic  $\text{AlCl}_3$ :EMIC solution vs. an aluminum metal counter electrode is shown in Figure 2. During the first 50 cycles, coulombic efficiency increased to over 98% while the capacity gradually faded. Similar measurements will be performed on other conductive polymers to determine the electrode materials with the highest voltage and capacity

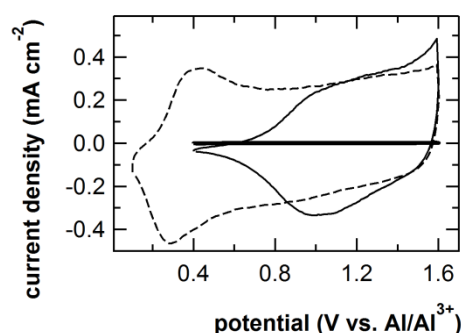
and the best cycling stability. Gravimetric or volumetric capacity of these materials in  $\text{AlCl}_3$ :EMIC will be determined by preparing and characterizing suspension-cast electrodes of chemically synthesized polymers.

## References

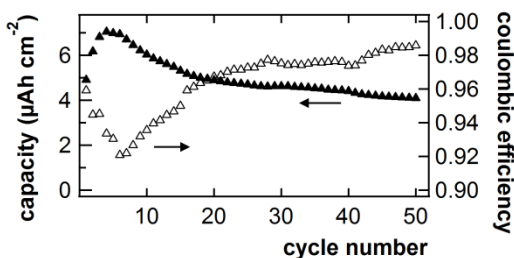
1. Q. F. Li and N. J. Bjerrum, *J Power Sources*, **110**, 1 (2002).
2. N. Jayaprakash, S. K. Das and L. A. Archer, *Chem Comm*, **47**, 12610 (2011).
3. J. J. Auborn and Y. L. Barberio, *J Electrochem Soc*, **132**, 598 (1985).
4. J. S. Wilkes, J. A. Levisky, R. A. Wilson and C. L. Hussey, *Inorg Chem*, **21**, 1263 (1982).
5. T. Jiang, M. J. C. Brym, G. Dube, A. Lasia and G. M. Brisard, *Surf Coat Tech*, **201**, 1 (2006).
6. P. G. Pickup and R. A. Osteryoung, *J Am Chem Soc*, **106**, 2294 (1984).
7. L. Janiszewska and R. A. Osteryoung, *J Electrochem Soc*, **134**, 2787 (1987).
8. N. Koura, H. Ejiri and K. Takeishi, *J Electrochem Soc*, **140**, 602 (1993).

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**Figure 1.** Cyclic voltammetry (CV) at  $10 \text{ mV s}^{-1}$  of polypyrrole (---), polythiophene (—), and glassy carbon substrate (—) in  $\text{AlCl}_3$ :EMIC (2:1 molar) at room temperature. Counter electrode and reference electrode are each aluminum metal.



**Figure 2.** Galvanostatic cycling at  $10 \mu\text{A cm}^{-2}$  of polythiophene film on glassy carbon substrate over voltage range  $0.6 - 1.6 \text{ V vs. Al/Al}^{3+}$ . Filled symbols: area-specific charge capacity; Unfilled symbols: coulombic efficiency. Other conditions are the same as in Figure 1.