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Electrodeposition of Silicon using Hexafluorosilicate Salts in Imidazolium Bromide

Summer 2003

Support was from The Experimental Program to Stimulate Competitive Research, EPSCoR (NSF), Alliance for Mintority Participation, AMP (NSF), and NASA.

The Noran Energy Dispersive Spectrometer (EDS), donated by Intel, was nearly brought to operation over the year. It turned out to have incorrect geometry for the JEOL 848 SEM. Due to the age of the instrument and lack of upgrades available, it was abandoned. EPSCoR funds purchased a Thermo Nicolet FTIR spectrometer with Inspect IR plus microscope at the end of the summer work. The entire team worked on the silicon project. The AMP students presented their work at the New Mexico State University Decade of Excellence conference October 2003. The AMP students, Cheryl Arviso and Brandy Marquez, won second place for best presentation at the conference.

The 2003 research team, Cheryl Aviso (biochemistry), Brandy Marquez (Engineering), David Gorm (Chemical Engineering), and Dr. Miller.

The team worked with a new compound, imidazolium bromide (IMZBr). IMZBr is part of the family of the so called organic ionic electrolytes which has been of interest in the electrochemical literature.

The EMIZBr was purchased from Aldrich. The melting point was found to be 68.5° C. The compound was found to be hydroscopic. The hexaflourosilicates we used in combination with our EMIZBr were: Na_2SiF_6 which had poor solubility in EMIZBr, $(NH_4)_2SiF_6$ which had a igher solubility in EMIZBr. We attempted to synthesize $(EMIZ)_2SiF_6$ using H_2SiF_6.

Attempted EMIZHFS Synthesis from EMIZBr

The metathesis reaction is

$2EMIZBr + H_2SiF_6 \quad ----> \quad (EMIZ)_2SiF_6 + 2HBr + H_2O$

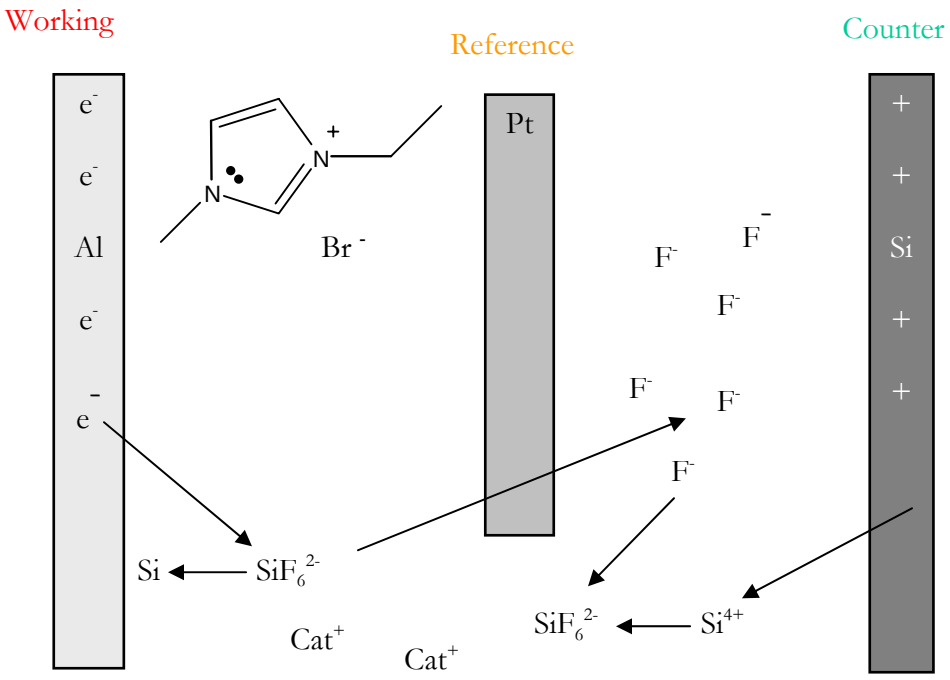
Stoichiometric amounts of EMIZBr and flourosilicic acid were added to a round bottom flask. In order to remove HBr and water, slight heating under vacuum was attempted. Not all the water and HBr could be removed. Nevertheless, some of this material was used in deposition experiments. We also tried 2-Methyl-2-Butene as an HBr getter.

$HBr + C_2H(CH_3)_3 \quad -----> \quad C_2H_2(CH_3)_3Br$

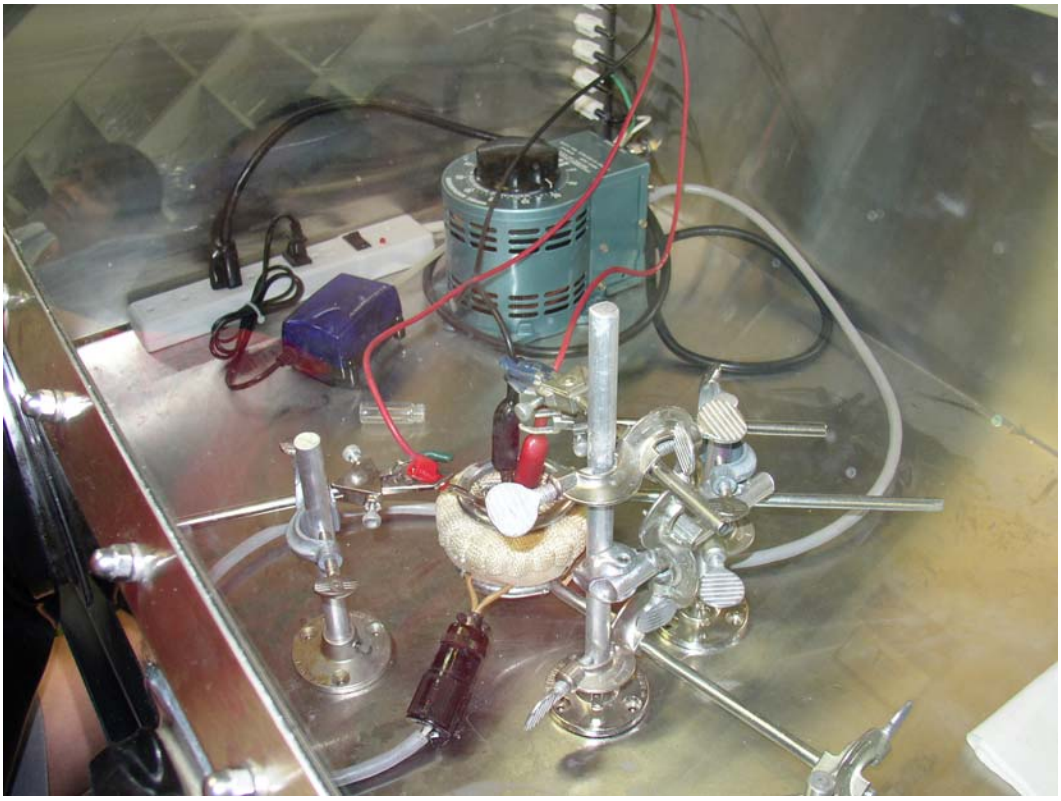
However, in attempting to reflux the mixture, the 2-Methyl-2-Butene would not mix well and would tend to vaporize leaving the mixture. This material still contained significant amounts of HBr.

Most of the experiments focused on ammonium hexafluorosilicate dissolved in imidazolium bromide.

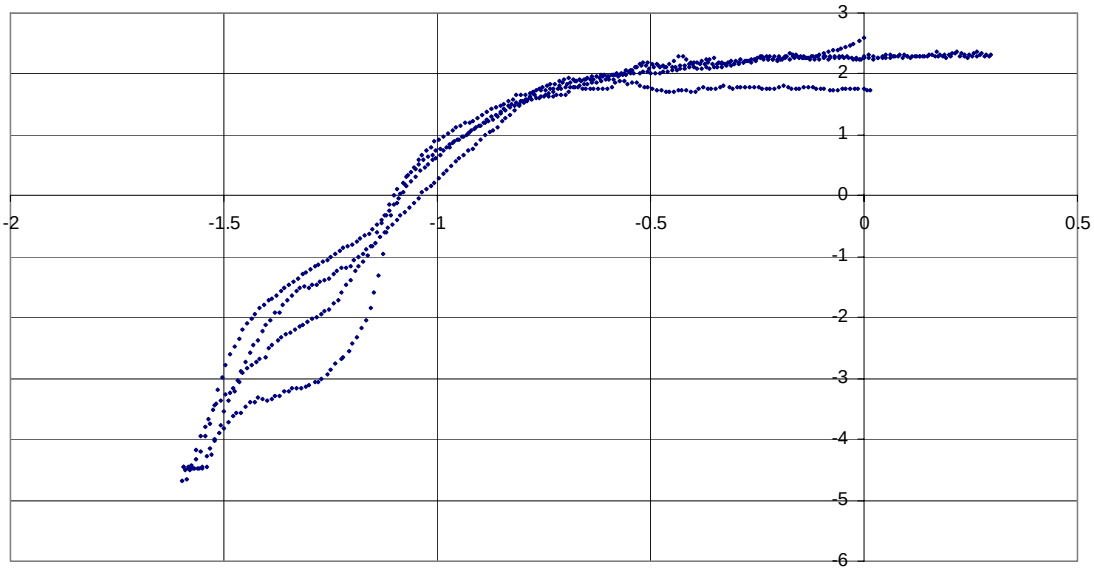
Electrochemistry Experiemnts



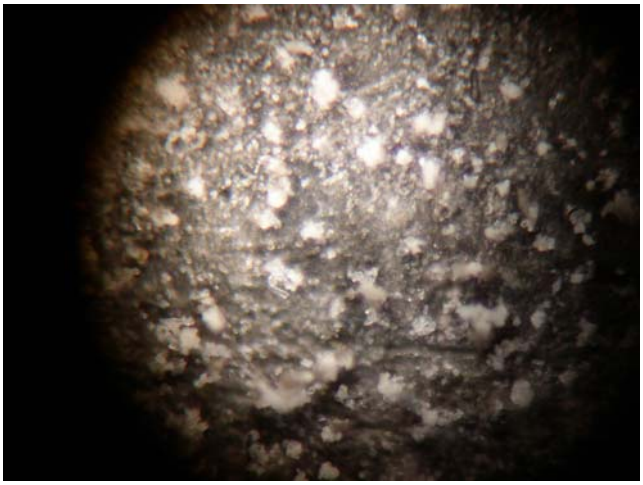
The above diagram shows schematically what we wanted to happen in the deposition cells. Experiments were run with ammonium hexafluorosilicate and sodium hexafluorosilicate dissolved in imidazolium bromide. We also ran experiments using the impure imidazolium hexafluorosilicate material described above. At the working electrode, held at negative potential, the hexafluorosilicate ion should be reduced to silicon. This releases fluoride ions in the solution. At the silicon counter electrode, silicon dissolves, picking up fluoride ions, reforming the hexafluorosilicate ion. CV experiments and potential step experiments were run at temperatures above but near the melting point of imidazolium bromide.



This is a typical cell set up in the TUI glove box under nitrogen scrubbed by copper turnings, dririte, and carbon columns.



Here is a cyclic voltammogram (cathodic potentials to the left) of 90% EMIZBR 10 %$(NH_4)_2SiF_6$ solution, upper limit: 300 mV; Lower limit: -1600 mV. Potential step experiments were run in the -1.5 volt range.



Micrograph of an aluminum electrode after a AHFS IMZBr potential step . Even at negative potentials, the aluminum was attacked ether by fluoride ions, bromide ions, or by single replacement with silicon. These were not the results we wanted. At this point it has been decided to abandon the use of hexafluorosilicate ions as a potential silicon source.