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Quantitative estimation of Bismuth (Bi) Plated Felts for Achieving Battery Efficiency of Fe-Cr Redox Flow

Dr. Shahbaz Khan

Professor, Department of Science and Humanities, Anjuman College of Engineering and Technology, Nagpur.

Email: drkhanshahbaz@gmail.com

Abstract: To catalyze Cr (iii)/Cr (ii) redox couple, bi turned into used as catlysts. Bi has an incredible conduct on discount and oxidation of chromium couple to decorate the performance of Fe-Cr redox flow cell. In this gift investigation catalysts carbon felt substrates were used as electrodes on poor side which had been electrochemically plated/ loaded with bi. A bathtub which include 10g / l Bi 2(So4)3 and 800g / l H_2So4 become established via electro-triumphing method. Felt samples have been used as cathodes, and anodes were used as inert graphite plates. To date $BiCl_3$ has been carried out as an element in anolyte to the electrolyte. Bi steel changed into electroplated in these studies on carbon felt surfaces that have been used as electrodes on the cell's bad side. The carbon felt electrode samples were plated with bi up to 12mg / cm2 further to h2o2 treatment and these were used in the bad (Cr) aspect of the rfb. Felt samples had been used as cathodes, and anodes have been used as inert graphite plates.

Key phrases: ***Fe-Cr redox flow cell, bi plated felts, PbCl2 as additive, chromium reduction efficiency coulombic efficiency***

1. INTRODUCTION:

The redox flow cell concept was proposed first in the 1970's. RFBs containing the Fe–Ti couple, where FeCl3 was used as the oxidizing agent and TiCl2 as the reducing agent, both couples were dissolved in an alkaline electrolyte. Ti2+ was replaced by Cr2+ leading to better performances during the years in 1980's. Redox flow batteries differ from conventional batteries because the active materials are concentrated solutions of redox-active solutes and not solid state materials. RFB is one type of an advanced rechargeable battery. One of the most attractive features is the possibility of an independent scaling of electric energy storage. Batteries generate electricity and store chemical energy by a redox (reduction/oxidation) reaction, as described above.

Galvanic cells, fuel cells and flow cells are all based on a redox reaction. Flow batteries (FB) are the second category of electrochemical storage systems. They are large energy storage devices that have a wide range of potential applications in a distributed generation network.

To overcome the problems associated with the Fe-Cr RFB was said and to commercialize the Fe-Cr RFB system with 100% Chromium redox efficiency, 98% Coulombic efficiency and maximum energy efficiency the following objectives were taken as scope of work. The Fe/Cr system has the problems, Cr ions electrode reaction is slow, because the different metal ions are used as positive and negative reactants; each ion is mixed through the membrane and thus gradually decrease the battery capacity. Cr ions redox potential is close to the hydrogen gas generation potential and a small amount of hydrogen gas is generated from the negative electrode near the end of the charge, thereby reducing the battery capacity because of differences in the SOC between the positive and negative electrodes.

In the present work, Bi electroplated carbon felts ware prepared as candidate electrodes for negative side of the cell. To date BiCl3 has been applied as an ingredient in anolyte to the electrolyte. Bi metal was electroplated in this research on carbon felt surfaces that were used as electrodes on the cell's negative side. The carbon felt electrode samples were plated with Bi up to 12mg / cm2 in addition to H2O2 treatment and these were used in the negative (Cr) side of the RFB, so that Fe-Cr RFB can be used as pilot plant research.

2. EXPERIMENTATION:

Chemicals and Reagents:

To execute this project several chemicals and reagents are used. Carbon felt was acquired from SGL Carbon Company, Germany, grade GFA-3, 3 mm thickness, graphite molds from Carbon Products, India. The chemicals KCl, K2CO3, CH3OH, 40% H2O2, HCl, FeCl2.6H2O, CrCl3.6H2O, Pb (CH3COO)2, 30% NH3 solution, CH3COONH4, BiCl3, H2SO4, Bi2(SO4)3, PbCl2, Bromocresol Green indicator, Ferroin indicator has been collected from Merck, India. Pb (Metal sheet) was obtained from DI Water and the central vendor.

Instrumentation used:

Ammeter, Voltmeter, Charger/Discharger, APLAB charger, Flow meters and CPVC piping, Double head pump. SEM –EDS, Spectrophotometer (Make: Systronics Model No: 2201), AAS.

Experimental setup:

The single cell that works with a double-headed pump that extracts electrolytes from the catholyte tank, and anolyte tank. Catholyte tank contains 1.3N $FeCl_2$ in 2N HCl and 1.3N $CrCl_3$, 0.05N $BiCl_3$ in 2N HCl is anolyte tank. Both the electrolytes pass through the respective chambers and consisting of graphite known as moulds. The carbon felt samples and are treated and Catalyzed and used as electrodes in moulds. The multifunction test machine controlled by the microprocessor serves as a charger and discharger. A gas flow meter was used to measure H2 gas which evolved in cell evaluation.

This redox flow batteries use complex setup with double head pump and flow meters. The piping of the RFB constructed with CPVC pipe fittings. Electrolyte tanks were prepared by polypropylene material. The redox flow cell Fe-Cr is made of an anolyte and a catholic. Both the pumped electrolytes into the corresponding compartments (molds). Constant current was supplied through the use of the terminals of the graphite moulds and dragged through electrodes. Electrodes select the load and convert the active materials as charged and discharged species by transferring protons via membrane. During physical examination, the dark parrot green catholyte transitions to the light brown colour when the cell reaches the 100% State of Charge (SOC) and the dark green anolyte changes to the satin blue colour. The cell was charged and discharged using a constant current supply. During charge, cell voltage was limited to 1.5V. During discharge care was taken (when necessary, the discharged current was reduced) to avoid cell reversal. For each charge/discharge cycle, the current and cell voltage were monitored.

The total charge passed and the ideal state of charge (assuming no side reactions) was determined from the Ampere-hour measurements. A series of charge/discharge cycles was performed for the electrodes which were given good results. The workability of our subscale full cell test equipment had been established with chloride electrolytes and sulphate electrolytes.

3. METHOD:

Method of bi-electroplating:

Fe-Cr RFB performance was significantly affected by the Cr(III)/Cr(II) redox couple reaction. To date BiCl3 has been applied as an ingredient in anolyte to the electrolyte. Bi metal was electroplated in this research on carbon felt surfaces that were used as electrodes on the cell's negative side. The carbon felt electrode samples were plated with Bi up to 12mg / cm2 in addition to H2O2 treatment and these were used in the negative (Cr) side of the RFB.

In this work, a bath consisting of 10g / L Bi2 (SO4)3 and 800g / L H2SO4 was established by electro-winning method. Felt samples were used as cathodes, and anodes were used as inert graphite plates. The respective electrical parameters (Ampere-Hour (Ah)) used to achieve 1 to 12 mg / cm2 Bi electroplated felt have been listed in Table-1 below.

Table 3.1: Electrical parameters given to produce Bi plated felts:

Catalyzed Bi electrode sample of 100 cm^2	**Required Bi (g)**	**Required Ah to electroplate Bi**	**Current (A)**	**Required time for plating (min)**
1 mg/cm^2 Bi felt	0.1	0.038	1	2.9
2 mg/ cm^2 Bi felt	0.2	0.076	1	5.7
4 mg/ cm^2 Bi felt	0.4	0.152	1	11.4
6 mg/ cm^2 Bi felt	0.6	0.228	1	17.1
8 mg/ cm^2 Bi felt	0.8	0.304	1	22.8
10 mg/ cm^2 Bi felt	1.0	0.380	1	28.5
12 mg/ cm^2 Bi felt	1.2	0.456	1	34.2

Method of cell Assembly:

Plating was carried out at a current density of 10 mA / cm^2. Coulombic efficiency of the
Process was 80%. For Nafion-117 PFSA proton exchange membrane, pre-treatment is needed to achieve good chemical properties and to eliminate cell resistivity. Membrane was pre-treated for 30 minutes in boiling DI water, followed by soaking for 15 minutes in 10 precent K2CO3 solution, and 0.6 M KCl solution for 2 hours.

Cell performance Measurement:

The cell was charged and discharged at a current density of 50 mA/cm^2. Variation in voltage was measured by connected multimeter. Chromium reduction efficiency (DCr) was measured by concentration of Cr (II) formation in anolyte, with respect to Ah parameter given, on the basis of 1N of 1 liter electrolyte needs 26.8 Ah value of current for one electron transfer reaction. The Faraday constant is the voltage on one mole of electrons equal to about 26.8 ampere- hours. It is used in electrochemical calculations.
DCr = (Normality of Cr (II)/ Normality of Cr (III)) X 100

4. RESULTS AND DISCUSSION:

Characterization of bi catalysed carbon felts:

Characterization of Bi plated samples was also carried out with SEM-EDS system. Fig.2 consists SEM images of the plated samples with Bi. Concentrations were 12 mg /cm2 in carbon felts respectively.

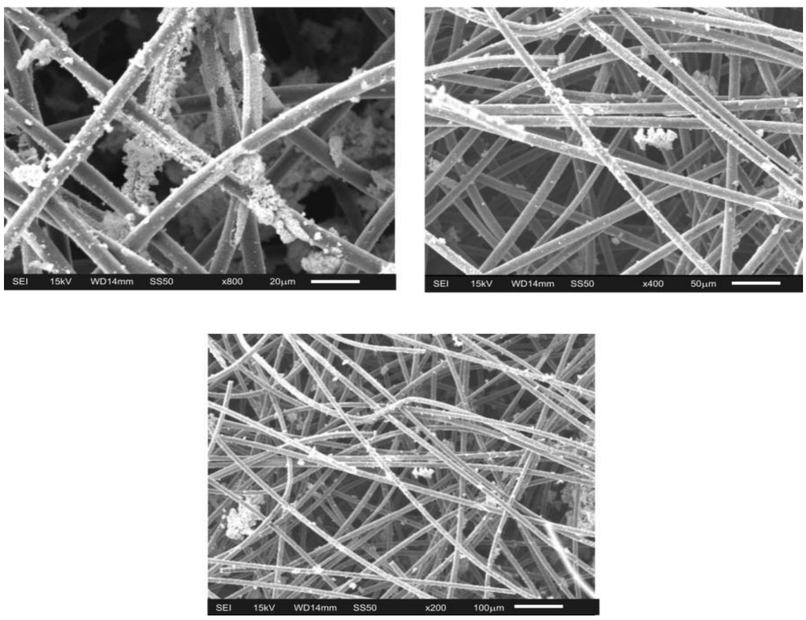


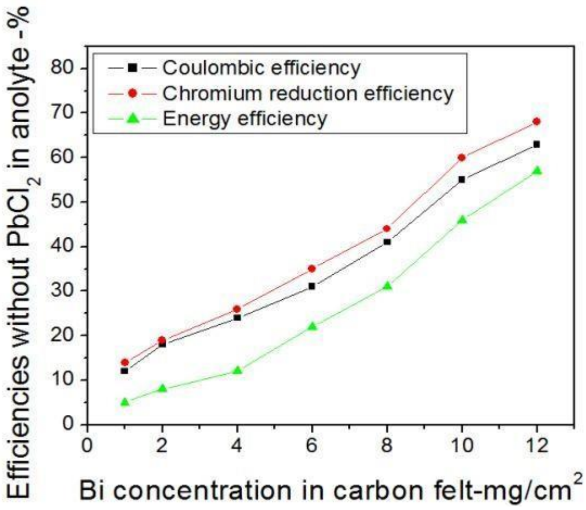
Fig.4.1: 12 mg/cm^2 Bi plated samples with different SEM resolution

By the SEM analysis it is confirmed that the Bi plating procedure not affected the carbon felt Structure. It is also confirmed that the plating of Bi on carbon felt was smooth and uniform. The images also states that, as Bi content increasing in the carbon felt the size of the carbon wire is also increasing uniformly. Fig.4.1 shows EDS spectra's obtained for 12 mg/cm2 plated felts of Bi.

Table 4.1: Efficiency results for varying Pb content in felt

Pb content in felt mg/cm^2	Chromium reduction Efficiency %	Columbic efficiency %	Energy efficiency %
1	12	14	5
2	18	9	8
4	24	26	12
6	31	35	22
8	41	44	31
10	55	60	46
12	63	68	57

Increasing trend of efficiency in chromium reduction and coulombic efficiency up to electrodes electroplated with Bi was observed. Experimental results shown in Fig.5 are tests of cells without the anolyte 0.01N PbCl2.



Graph 4.1: Efficiencies without PbCl2 in anolyte

5. CONCLUSION:

Characterization of Bi metal electroplated carbon felt samples with SEM-EDS system was achieved. Cell performance of Bi Catalyzed carbon felt and PbCl2 as additive in anolyte observed were 100% DCr, 96% DC and 65% DE achieved. The methodology applied to load Bismuth metal on carbon felts with present method was entirely satisfactory. The adopted method for electro-winning Bi metal holds good for pilot plant research. Since the catalysis is achieved at 32°C, heating of electrolytes not required.

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