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Measurement Of Bi-Plated Felts For Achieving Battery Efficiency Of Fe- Cr Redox Flow

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Abstract

To catalyze Cr(III)/Cr(II) redox couple, Bi was used as catlysts. Bi has a remarkable behavior on reduction and oxidation of chromium couple to enhance the performance of Fe-Cr redox flow cell.In this present investigation catalysts *carbon felt substrates were used as electrodes on negative side which were electrochemically plated/ loaded with Bi.* A bath consisting of 10g / L $Bi_2(SO_4)_3$ and 800g / L H_2SO_4 was established by electro-winning method. Felt samples were used as cathodes, and anodes were used as inert graphite plates. To date $BiCl_3$ 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 / cm^2 in addition to H_2O_2 treatment and these were used in the negative (Cr) side of the RFB. Felt samples were used as cathodes, and anodes were used as inert graphite plates.

Keywords: *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 by NASA in the 1970's, especially where the NASA group became active in different projects. 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. Ti^{2+} was replaced by Cr^{2+} 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

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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.

The principle of the RFB system was presented by L. H. Thaller (NASA) of the United States in 1974. NASA mainly conducted research on the Fe/Cr system, discontinuing it in 1984 with the publication of the Final Report. At the same time in Japan, the Electro Technical Lab. (ETL; currently the National Institute of Advanced Industrial Science and Technology) was conducting basic research, and the development of the Fe/Cr system made progress as a project of the New Energy and Industrial Technology Development Organization (NEDO). In about 1985, in Australia, the University of New South Wales (UNSW) proceeded to develop the Vanadium system. Concerning the practical use of RF batteries, electric power companies and manufacturers in Japan jointly conducted research with enthusiasm, and in about 2001, the Vanadium system was partially put into practical use.

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 / cm^2 in addition to H_2O_2 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.

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2. EXPERIMENTATION

2.1. 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 [1], graphite molds from Assam Carbon Products, India, and Dupont, USA, Nafion-117 PFSA Membrane imported form [2]. The chemicals KCl, K_2CO_3, CH_3OH, 40% H_2O_2, HCl, $FeCl_2.6H_2O$, $CrCl_3.6H_2O$, Pb $(CH_3COO)_2$, 30% NH3 solution, CH_3COONH_4, $BiCl_3$, H_2SO_4, $Bi_2(SO4)_3$, $PbCl_2$, Bromocresol Green indicator, Ferroin indicator has been collected from Merck, India. Pb (Metal sheet) was obtained from DI Water and the central vendor.

2.2 INSTRUMENTATION USED:

Ammeter, Voltmeter, Charger/Discharger ((Xin Ke Hua co., Ltd., Model No: MTL-C), APLAB charger, Flow meters and CPVC piping, Double head pump,. SEM -EDS (JEOL make, Model No: JSM 6610LV), Spectrophotometer (Make: Systronics Model No:2201), AAS.

2.3 EXPERIMENTAL SETUP

Redox flow cell setup schematics were shown in Fig.1. The single cell that works with a double-headed pump (3) that extracts electrolytes from the catholyte tank (1) and anolyte tank (2). Catholyte tank contains 1.3N $FeCl_2$ in 2N HCl and 1.3N $CrCl_3$, 0.05N BiCl3 in 2N HCl is anolyte tank. Both the electrolytes pass through the respective chambers (4) and (5) consisting of graphite known as moulds. The carbon felt samples (6) and (7) are treated and catalyzed and used as electrodes in moulds. The cell consists of a separator (8) (Nafion-117 PFSA membrane) which is a proton exchange membrane, enabling only protons to exchange load balance in the cell through all of it. The multifunction test machine (9) controlled by the microprocessor (Xin Ke Hua Co., Ltd., Model No: MTL-C) serves as a charger and discharger. A gas flow meter (10) (Toshniwal) was used to measure H_2 gas which evolved in cell evaluation.

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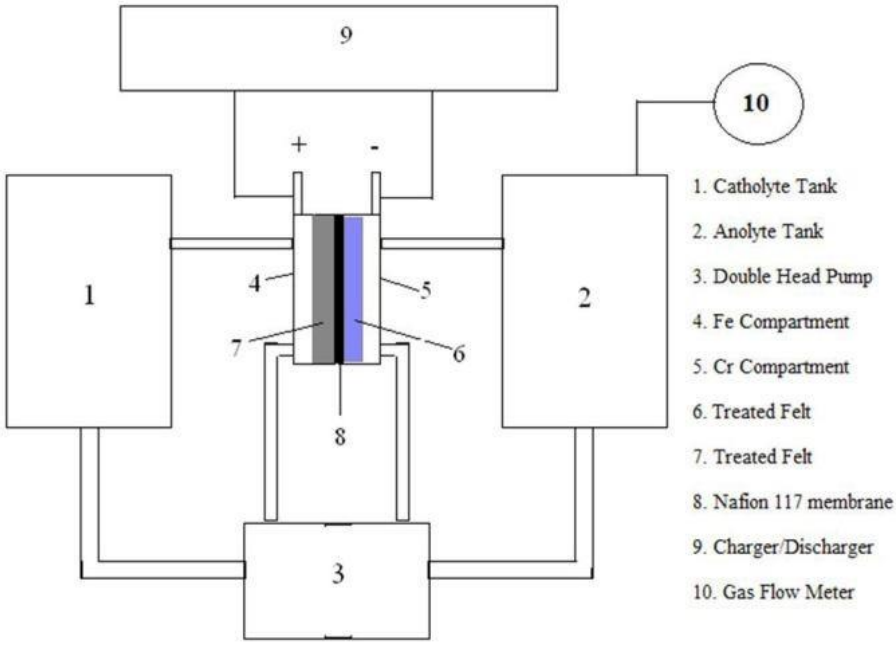

Fig..1: Schematic diagram of redox flow cell setup

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 color when the cell reaches the 100% State of Charge (SOC) and the dark green anolyte changes to the satin blue color. 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.

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3. METHODS

3.1 M ETHOD OF Bi-ELECTROPLATING

Fe-Cr RFB performance was significantly affected by the Cr(III)/Cr(II) redox couple reaction. To date $BiCl_3$ 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 / cm^2 in addition to H_2O_2 treatment and these were used in the negative (Cr) side of the RFB.

In this work, a bath consisting of 10g / L $Bi_2(SO4)_3$ and 800g / L H_2SO_4 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 / cm^2 Bi electroplated felt have been listed in Table-1 below.

Table-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

Plating was carried out at a current density of 10 mA / cm^2. Coulombic efficiency of the process was 80% [3].

3.2 NAFION-117 M EMBRANE PRETREATMENT:

For Nafion-117 PFSA proton exchange membrane, pretreatment is needed to achieve good chemical properties and to eliminate cell resistivity. Membrane was pretreated for 30 minutes in boiling DI water, followed by soaking for 15 minutes in 10 percent K_2CO_3 solution, and 0.6 M KCl solution for 2 hours [4].

3.3 NAFION-117 M EMBRANE POST-TREATM ENT :

Due to evaluation of cell, it will be exposed to ferric chloride solution. This can cause a fouling effect to membrane by forming metal complexes with available chlorine ions which

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were in electrolyte. Upon completion of the cell assessment membranes were soaked as post treatment in 2N HCl to mitigate the fouling effect [5].

3.4 M ETHOD OF CELL ASSEMBLY

Such Pb electroplated felts were used as Cr-side electrodes and Fe-side electrodes were used as H_2O_2 treated felts. Treated and catalyzed felt was placed in graphite moulds, and the layer between them was placed. Using sleeved screws molds is tightened then the cell was put in the test configuration.

The positive electrolyte was 5 liter of 1.3M FeCl2 in 2N HCl. The negative electrolyte was 5liter of 1.3M $CrCl_3$ in 2N HCl. For electrocatalysis, the anolyte solution was saturated with PbCl2. Active electrode area was 100 cm^2. A H2O2 cleaned carbon felt served as an inert electrode on the positive side of the cell, while a catalyzed carbon felt as an inert electrode on the negative side of the cell. Nafion-117 PFSA proton exchange membrane was used as a separator. Each flow-through carbon felt electrode was gasketed with a piece of 0.05" thick polyethylene sheet cut to the appropriate shape. Two wax-impregnated graphite moulds completed the sandwich cell. The sandwich was held together by running a series of sleeved bolts completely through the sandwich at its edges and tightening with nuts.

3.5 MEASUREM ENT OF CELL PERFORMANCE

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. [6].

DCr = (Normality of Cr(II)/ Normality of Cr(III))* 100

Coulombic efficiency (DC) of the cell was measured by input Ah and output Ah while charge and discharge.

DC = (output Ah/ input Ah) * 100

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Energy efficiency (DE) was measured on the basis of input and output values of current and voltage while charge and discharge.

DE = [(output current* average output Voltage) / (input current*average input Voltage)]*100

The electrochemical behavior of synthesized catalyzed carbon felts were also evaluated for Hydrogen generation while charging the cell. The anolyte tank was connected to a gas flow meter, H_2 gas evolved was measured with respect to time in the parameter liter per hour.

4. RESULTS AND DISCUSSION

4.1 CHARACTERIZATION OF BI CATALYZED 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 was 12 mg /cm^2 in carbon felts respectively.

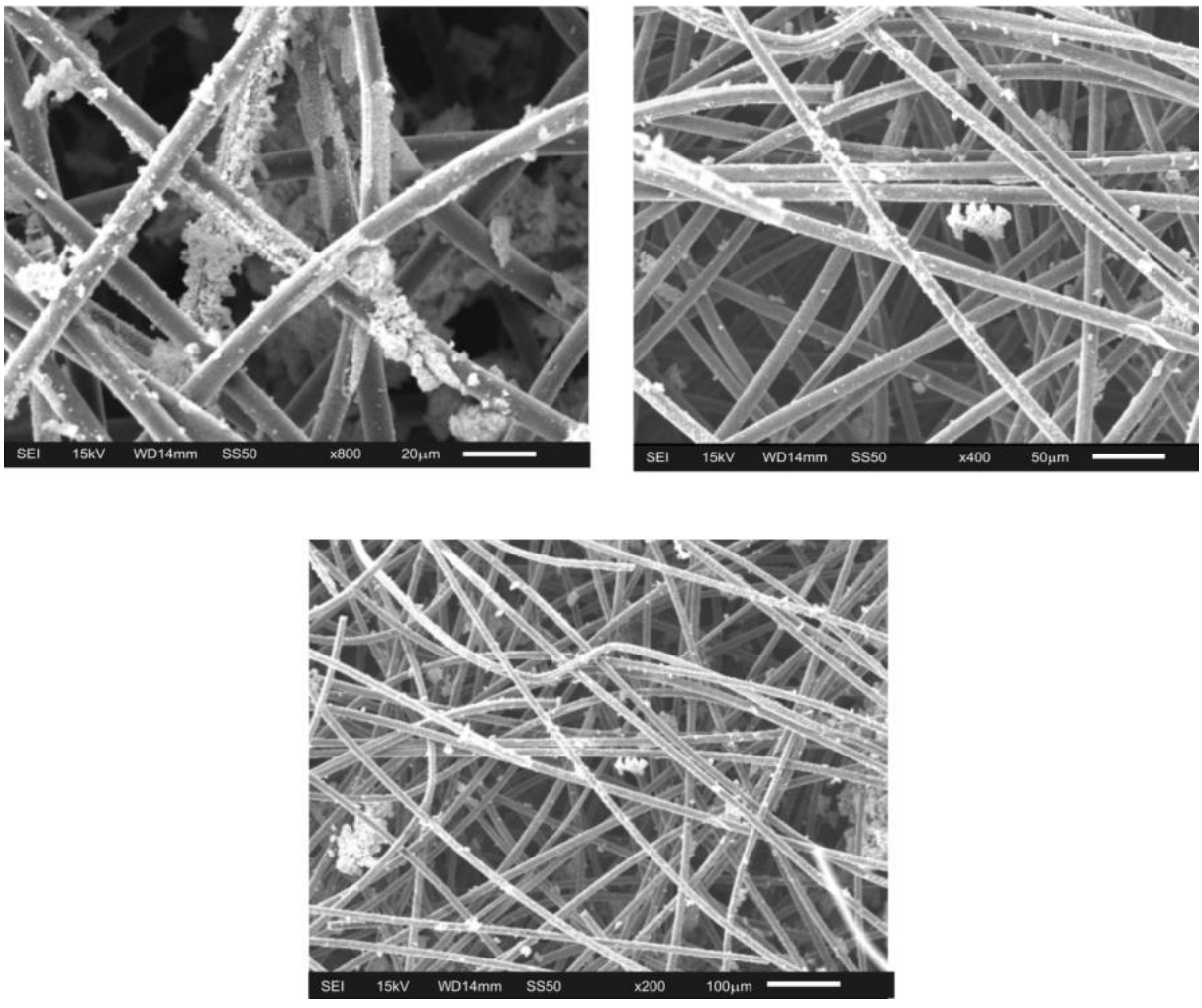

Fig.2 : 12 mg/cm^2 Bi plated samples with different SEM resolution.

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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.2. shows EDS spectras obtained for 12 mg/cm^2 plated felts of Bi.

4.2 CHARACTERIZATION OF BI CATALYZED FELTS WITH EDS

To confirm the Bi content in felt EDS analysis was carried out. The following images were EDS spectra obtained from the analysis.

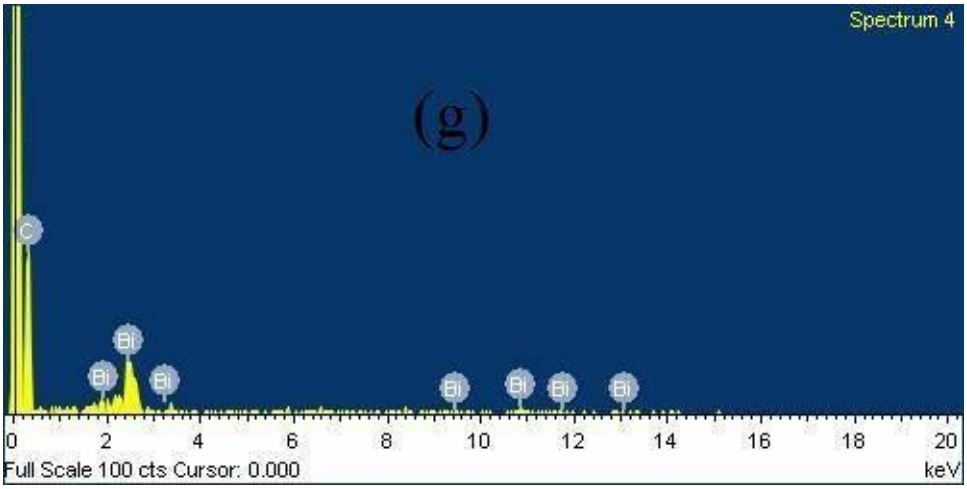

Fig.3 are EDS spectrums of Bi plated felts

EDS spectras shown corresponding characteristic Bi peaks. As Bi concentration in samples was increasing the corresponding peaks are also improved till the concentration reaches maximum as 12 mg/cm^{2}s.

4.3 Bi-PLATED FELTS AS ELECTRODES WITH CHLORIDE ANOLYTE

In order to suppress the evolution of hydrogen gas and to know the necessary practical catalytic concentration of Bi, the cell assessments were initially carried out in anolyte without $PbCl_2$. Hydrogen gas suppression was found with regards to Bi concentration in felt, but with Bi content of 12 mg / cm^2 the cell developed 0.4Lt./hour H_2 gas. More experiments in anolyte were conducted with 0.01N $PbCl_2$. The combination resulted in less hydrogen gas

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starting with 0.5 mg / cm^2 felt and no hydrogen gas developed after 8mg / cm^2 of Bi concentration. Results were given in Table-2.

Table 2: H2 gas evolved with and without PbCl2 as additive

Bi content in felt mg/cm^2	H2 gassing without PbCl2 in additive Lt./Hr	H2 gassing with PbCl2 in additive Lt./Hr
1	1.1	0.31
2	0.95	0.26
4	0.76	0.14
6	0.63	0.05
8	0.54	0
10	0.47	0
12	0.4	0

Results of hydrogen evolution with and without the additive $PbCl_2$ in anolyte for the electrodes which were electroplated with Bi from 1 to 12 mg / cm^2 were shown Fig.4.

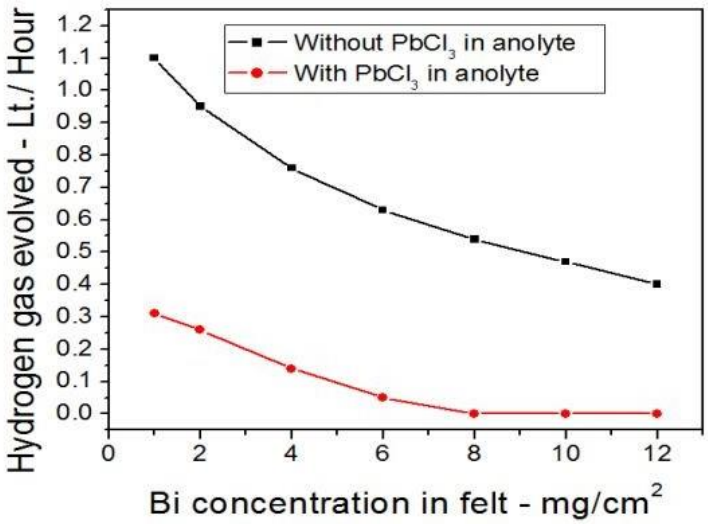

Fig.4: Results of H2 gas evolved with and without 0.01N PbCl2 in anolyte.

The efficiency of the Chromium redox reaction was calculated by charging and discharging the cell at constant current. For the felt containing 12 mg / cm^2 Bi content, these experiments were also conducted with and without $PbCl_2$ in anolyte, a maximum efficiency of 68 percent

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chromium reduction, 63 percent coulombic efficiency and 57 per cent energy efficiency. See Table-3 for results

Table-3: Efficiency results for varying Pb content in felt

Pb content in felt mg/cm^2	Chromium reduction efficiency %	Coulombic 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 $PbCl_2$.

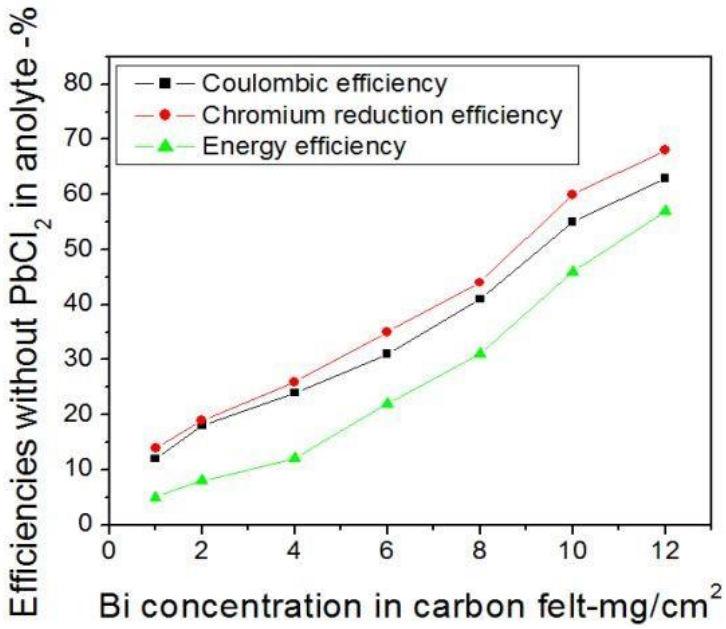

Fig.5: Efficiencies without PbCl2 in anolyte

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While the experiments with 0.01N PbCl2 in anolyte has observed 100% chromium reduction efficiency, 96% coulombic efficiency and 65% energy efficiency when the Bi concentration in the carbon felt was 8mg/cm^2. Cell results were given in Table-4.

Table-4: Efficiencies with PbCl2 in anolyte

BiCl3 in anolyte mg/cm^2	Coulombic efficiency %	Chromium reduction efficiency %	Energy Efficiency %
1	59	63	33
2	65	69	38
4	69	78	44
6	76	89	51
8	85	100	57
10	92	100	61
12	96	100	65

Cell results with 0.01N PbCl2 as additive in anolyte were given in Table-4. Results were shown in graphically in Fig.6.

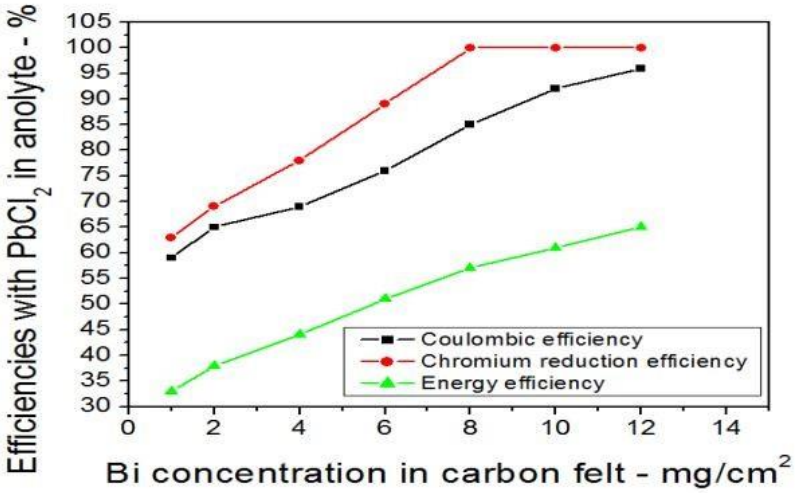

Fig.6: Efficiencies with PbCl2 in anolyte

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This growing trend can be stated on the basis of Bi metal's surface catalytic properties, conducts as an electron mediator from electrode to chromium so that chromium reduction is much easier and Pb metal tends to develop chloride-ion complexes in solution phase as $[PbCl_3]$-and $[PbCl_4]_2$- stabilize the $CrCl_2$ developed in the solution while charging the cell[7].

Changing the anolyte color from dark green to satin blue indicates achieving 100% SOC and 100% reduction in chromium. Coulombic efficiency was calculated and extracted from the cell as per the Ampere-Hour. Energy efficiency was determined by voltage levels and current density while the cell was being charged and discharged[8].

5. CONCLUSION

Characterization of Bi metal electroplated carbon felt samples with SEM-EDS system was achieved. Cell performance of Bi catalyzed carbon felt and $PbCl_2$ as additive in anolyte observed were 100% D_{Cr}, 96% D_C and 65% D_E achieved. The methodology applied to load Bi 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 32oC, heating of electrolytes not required.

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