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Enhancement of Reversibility of Cr(III)/Cr(II) Redox Couple In Fe-Cr Flow Cell with Bi-Pb Electroplated Carbon Felts

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Abstract: *Improvisation of Fe-Cr redox flow cell performance was significantly related to reversibility of the Cr(III)/ Cr(II) redox couple. To catalyze this redox reaction Bi and Pb metals were electroplated on carbon felt for reduction and oxidation of chromium. To achieve a better performance of redox flow cell these electroplated carbon felts are used on negative side of the flow cell. The flow cell experiments are carried out with only Bi electroplated felts using 0.01N $PbCl_2$ as additive in anolyte and another carbon felts are electroplated with the combination of Bi-Pb and used on negative side of the cell without any additive. The experimental results observed that the Bi electroplated felts with $PbCl_2$ additive shows 100% chromium reduction efficiency, 96% coulombic efficiency and 65% energy efficiency. While Bi and Pb combination felts without any additive has shown 100% chromium reduction efficiency, 98% coulombic efficiency and 72% energy efficiency. The cell operated with 5 liters of electrolytes containing 1.3N active materials dissolved in 2N HCl solution. 100 cm^2 carbon felt samples were utilized as electrodes at a current density of 50 mA/ cm^2. Nafion-117 PFSA membrane was used as a separator because of its high chemical and mechanical stability.*

Key words - *Bi-Pb electroplated felts, Chromium reduction efficiency, Coulombic efficiency, Energy efficiency, Fe-Cr Redox flow cell.*

I. Introduction

The stationary energy storage system, Redox Flow Battery (RFB) was first studied and developed by NASA. These systems are explored with renewable energy resources like solar photo voltaic cells for energy storage [1-3]. RFB's are able to give required output of power or voltage by connecting the cells in parallel or series by stacking [4]. While increasing the volume of the electrolytes in external storage tanks the energy capacity can be scaled up as required, these features makes RFB's attractive candidates for large scale stationary storage applications [5-6].

However, the problem of enhancing the efficiency of Fe-Cr RFB is directly related with reversibility of redox couple Cr(III)/Cr(II). The carbon felt electrode with low current densities like 40 mA/cm^2 was used to achieve this. To improvise the performance of redox couple many researchers were added their efforts. As received the carbon felt substrates were not used as electrodes for the cell operation [7-11]. They have to be pre-treated for normalization to attain good chemical properties, to catalyze the chromium redox couple. However, the literature shown that thermodynamically hydrogen has evolved before chromium is reduced. Evolution of hydrogen reduces the coulombic efficiency of the system and over a period of cycles, allows the system to become chemically out of balance thus loses its effective capacity. Pre-cleaning processes for carbon felts were executed with H_2SO_4, KOH and HNO_3 to attain good redox properties as well as less hydrogen gassing [12, 13]. In addition to normalization treatments sufficient catalysts are needed in anolyte to improve the redox reaction of chromium and to decrease the hydrogen over potential. Au catalytic treatment for carbon felts and addition of $PbCl_2$ and $BiCl_3$ in anolyte was first suggested by NASA [14, 15]. Combination of Pb, Au, Bi and Tl, thermally impregnated in carbon felts to improve the performance of Fe-Cr RFB was also studied [16]. But considerable coulombic, chromium redox reaction efficiency and energy efficiencies were not achieved by the above processes. Maximum coulombic efficiency reported was 97% [17].

Present research was study on electroplated carbon felts with 1-12 mg/cm^2 Bi as candidate electrode and used on negative side of the cell with 0.01N $PbCl_2$ as additive in anolyte. Electrode possessing 8mg/cm^2 Bi and 0.01N $PbCl_2$ in anolyte was yielded considerable results. A further study was also performed with the combination of Bi-Pb electroplated felts to improve the performance of the cell. Bi-Pb combination felts were trailed and examined for zero hydrogen gassing, 100% chromium reduction efficiency, maximum coulombic and energy efficiencies, So that to use Fe-Cr redox couple as bulk energy storage system for load leveling & stand-alone applications.

II. Experimentation

2.1 Materials & Reagents

Carbon felt (M/s SGL carbon, Germany), Graphite Moulds, Nafion-117 PFSA Membrane (Dupont, USA), KCl, K_2CO_3, CH_3OH, 40% H_2O_2, Pb (Metal sheet), Pb $(CH_3COO)_2$, 30% NH_3 solution, CH_3COONH_4, H_2SO_4, $Bi_2(SO_4)_3$, HCl, $FeCl_2.6H_2O$, $CrCl_3.6H_2O$, $PbCl_2$ and DI Water.

2.2 Instrumentation

Evaluation of Bi and Bi-Pb uniform dispersion and amount of Bi and Pb plated on carbon felts was done by SEM-EDS system (Make: JEOL, Model No: JSM6610LV). Concentration of electrolytes was measured by a double beam UV-Vis spectrophotometer (Make: Systronics, Model No: 2201) [18].

2.3 Test setup

Schematic of redox flow cell setup was shown in Fig.1. The single cell working with a double head pump (3) which pumps the electrolytes from catholyte tank (1) and anolyte tank (2). Catholyte tank comprises 1.3N $FeCl_2$ in 2N HCl and anolyte tank comprises 1.3N $CrCl_3$ in 2N HCl. Both the electrolytes pass through the respective chambers (4) and (5) made up of graphite called as moulds. The catalyzed and treated carbon felt samples (6) and (7) are used as electrodes in moulds. The cell comprises a separator (8) (Nafion-117 PFSA membrane) which is proton exchange membrane, allows only proton to exchange through it for charge balance in the cell. Microprocessor controlled multifunction test machine (9) (Xin Ke Hua co., Ltd., Model No: MTL-C) serves as a charger and discharger. Measurement of H_2 gas which was evolved in cell evaluation was done using a gas flow meter (10) (Toshniwal).

2.4 Procedure

2.4.1 Procedure for pre-treatment of carbon felt

The roll of the carbon felt actually available size is 330X330X3 mm, was divided into pieces of 10X10 cm, which was used as electrode (100 cm^2). Carbon felts as received will have high surface tension initially; hence they were cleaned in methanol for 10 minutes, which makes the entire surface area active and available for cleaning. These cleaned felts were dipped in 40% H_2O_2 for 48 hours to normalize the felt by oxidizing the excess reducing groups in it [19]. Then felt samples were washed in DI water until the pH≈7 and dried at 200^oC for 3 hours in a hot air oven. This pre-treated carbon felt samples were used as electrodes on positive (Fe) side directly.

2.4.2 Procedure for Bi Electroplated carbon felts

In addition to H_2O_2 treatment the carbon felt electrode samples were plated with Bi up to 12mg/cm^2 and these were used in negative (Cr) side of the RFB. In this work Bi plating was established by electro-winning method, by preparing a bath consisting 10g/L $Bi_2(SO_4)_3$ and 800g/L H_2SO_4. Felt samples were used as cathodes and inert graphite plates were used as anodes. The respective electrical parameters (Ampere-Hour (Ah)) given to attain 1 to 12 mg/cm^2 Bi electroplated felts were mentioned in TABLE-1. Plating was carried out at a current density of 10 mA / cm^2. Coulombic efficiency of the process was 80% [20].

2.4.3 Procedure for Bi-Pb Electroplated carbon felts

After Bi plating the same felt samples were plated with Pb in a bath consisting 400g of lead acetate and 400g of ammonium acetate in one liter of DI water. Bi plated electrodes were initially dipped in 30% ammonia solution for 2 minutes and placed in bath, by giving negative charge. Pb metal sheets were utilized as anodes. Soluble Pb metal sheets were used as anodes to keep bath free of PbO_2. Pb Plating was carried out at a current density of 10 mA / cm^2. To get 1 to 12 mg/cm^2 Pb electroplated felts, the respective current and time (Ah) information was mentioned in TABLE-2. The value of time in minutes was corrected according to coulombic efficiency of the process (92%). By using 30% ammonia solution bath pH was maintained at 11 throughout the plating experimentation.

2.4.2 Procedure for pre-treatment of Nafion-117 PFSA membrane

To attain good chemical properties and to minimize the resistivity of the cell, pre-treatment is required for proton exchange membrane. Membrane was pretreated in boiling DI water for 30 minutes, followed by soaking in 10% K_2CO_3 solution for 15 minutes and 0.6M KCl solution for 2 hours [21]. After completion of cell evaluation membranes were soaked in 2N HCl as post treatment to minimize the fouling effect.

2.4.3 Procedure for cell assembly

These Bi and Bi-Pb electroplated felts were utilized as electrodes on negative (Cr) side and H_2O_2 treated felts were used as electrodes on positive (Fe) side. Treated and catalyzed felts were placed in graphite

moulds and membrane was placed between them. Moulds were tightened with sleeved screws. The cell was then placed in test setup.

2.4.4 Procedure for cell evaluation

Fe-Cr redox flow cell comprises an anolyte and catholyte. Both the electrolytes pumped in to respective compartments (moulds). By using the terminals of the graphite moulds constant current was supplied and dragged through electrodes. Electrodes pick the charge and convert the active materials as charged and discharged species. Balancing of the cell was done by Nafion-117 PFSA membrane by transferring protons from one side to another side. During physical observation, when cell achieves the 100% State Of Charge (SOC) the dark parrot green colour catholyte changes to light brown colour and dark green colour anolyte changes to satin blue colour. This colour change can appear brightly when the cell achieves minimum of 90% SOC.

III. Results & Discussion

3.1 Characterization of electrodes

The electrochemical plating of Bi and Bi-Pb on carbon felts was carried out from 1 to 12 mg/cm^2 and in which 8 mg/cm^2 Bi-Pb (each) sample was shown high coulombic and chromium reduction efficiency. To determine the uniform dispersion of the Bi-Pb in carbon felts, sample was examined by Scanning Electron Microscope (SEM). The SEM image shows that there is a uniform dispersion of Bi-Pb content. Treated carbon felt and Bi-Pb plated carbon felt SEM images were shown in Fig.2. Total Bi-Pb content in carbon felt was examined by EDS graph was shown in Fig.3.

3.2 Evaluation of electrodes

The performance of the electrodes prepared by above methods has been investigated basing on suppression of hydrogen gas evolution, chromium redox reaction and its single-cell characteristics. Evaluations are based on charging of the cell to 100% SOC and discharging. Cell evaluations are performed at a constant current density of 50 mA/ cm^2.

To suppress the hydrogen gas evolution and to know the required practical catalytic concentration of Bi, the cell evaluations were carried out without $PbCl_2$ in anolyte initially. Hydrogen gas suppression was observed with respect to the concentration of Bi in felt, Even though, the cell evolved 0.4 L/Hour hydrogen gas which is using 12 mg/cm^2 Bi catalyzed felt. Further experiments were carried out with 0.01N $PbCl_2$ in anolyte. The combination resulted less hydrogen gassing starting with 1 mg/cm^2 felt and no hydrogen gas was evolved after the Bi concentration reached to 8 mg/cm^2. Results of hydrogen evolution for the electrodes which were electroplated with Bi from 1 to 10 mg/cm^2 with and without the additive $PbCl_2$ in anolyte were shown in Fig.4.

Chromium redox reaction efficiency was estimated by charging and discharging the cell at a constant current. These experiments also carried out with and without $PbCl_2$ in anolyte. Without $PbCl_2$ in anolyte a maximum of 68% chromium reduction efficiency, 63% coulombic efficiency and 57% energy efficiency was recorded for the felt which was containing 12 mg/cm^2 Bi content. Increasing trend of chromium reduction efficiency and coulombic efficiency was observed for the electrodes which were electroplated with Bi, while the experiments with 0.01N $PbCl_2$ 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. Experimental results were shown in Fig.5 are without the 0.01N $PbCl_2$ in anolyte and the results of cell with 0.01N $PbCl_2$ additive in anolyte were shown in Fig.6.

This increasing trend can be explained based on the surface catalytic properties of Bi metal, acts as electron mediator from electrode to the chromium so that reduction of chromium much easier and Pb metal is having tendency to form chloro-complexes with chloride ion in solution phase as $[PbCl_3]^-$ and $[PbCl_4]^{2-}$ to stabilize the $CrCl_2$ formed in the solution, while charging of the cell [22].

Colour change of anolyte from dark green to satin blue indicates the achievement of 100% SOC and 100% chromium reduction. Coulombic efficiency was measured according to Ampere-Hour given and taken out from the cell. Energy efficiency was calculated by the values of voltage and current density while charge and discharge of the cell [23].

A further study was carried out for improvising the coulombic and energy efficiencies with combination of Bi-Pb electroplated felts. The felts were prepared by fixing the concentration of the Bi in felts at 8 mg/cm^2 while the concentration of Pb was varied from 1 to 12 mg/cm^2. Increasing trend of the coulombic and energy efficiencies was observed till the concentration of Bi-Pb (Each) was 8mg/cm^2. After that the effect of concentration of Pb in felt was meager. A maximum of 100% chromium reduction efficiency, 98% coulombic efficiency and 72% energy efficiency values were recorded. Results were shown in Fig.7.

To check this electrode performance and reproducibility an evaluation was carried out by 15 cycles of charge and discharge and monitoring the chromium reduction efficiency, coulombic efficiency and energy efficiency. The results indicated that the electrodes prepared by 8mg/cm^2 each of Bi and Pb carbon felts shown

98-100% chromium reduction efficiency, 96-98% coulombic efficiency, without hydrogen gassing evolution and maximum energy efficiency recorded was 72%. These results were shown in Fig.8.

The reduction potential for Bi is more electropositive than Pb, and this makes Bi more stable catalyst component than Pb. Bi oxidizes near the chromium electrode standard potential, so Bi will not go into solution until the total $CrCl_2$ converts to $CrCl_3$. Therefore while Pb tends to deplete from the electrode at low SOC, typical cell cycling would not cause Bi to go into solution during discharge [24].

IV. Conclusions

1. The methodology to plate Bi metal to carbon felts was entirely satisfactory at temperature 100^oC.
2. The process implemented to plate Pb metal to carbon felts was entirely satisfactory at pH 11 at room temperature (32^oC).
3. Achieved 100% chromium reduction efficiency, 98% coulombic efficiency and 72% energy efficiency for the Fe-Cr redox flow cell with $8mg/cm^2$ Bi-Pb content each.
4. It is confirmed that H_2O_2 treated carbon felt possessing Bi-Pb up to 8 mg/cm^2 each is practical electrode for the negative side of the Fe-Cr redox flow cell at room temperature (32^oC), so that heating of the electrolytes was not required.
5. The catalyzed felts were utilized for the single cell evaluations with an electrode area of 100 cm^2 at a current density of 50 mA/ cm^2.

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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

Table-2: Electrical parameters given to produce Pb plated felts

Catalyzed Pb electrode sample of 100 cm^2	Required Pb (g)	Required Ah to electroplate Pb	Current (A)	Required time for plating (min)
1 mg/cm^2	0.10	0.026	1	1.8
2 mg/cm^2	0.20	0.052	1	3.6
4 mg/cm^2	0.40	0.103	1	7.2
6 mg/cm^2	0.60	0.155	1	10.8
8 mg/cm^2	0.80	0.207	1	14.4
10 mg/cm^2	1.00	0.259	1	18.0
12 mg/cm^2	1.20	0.310	1	21.6

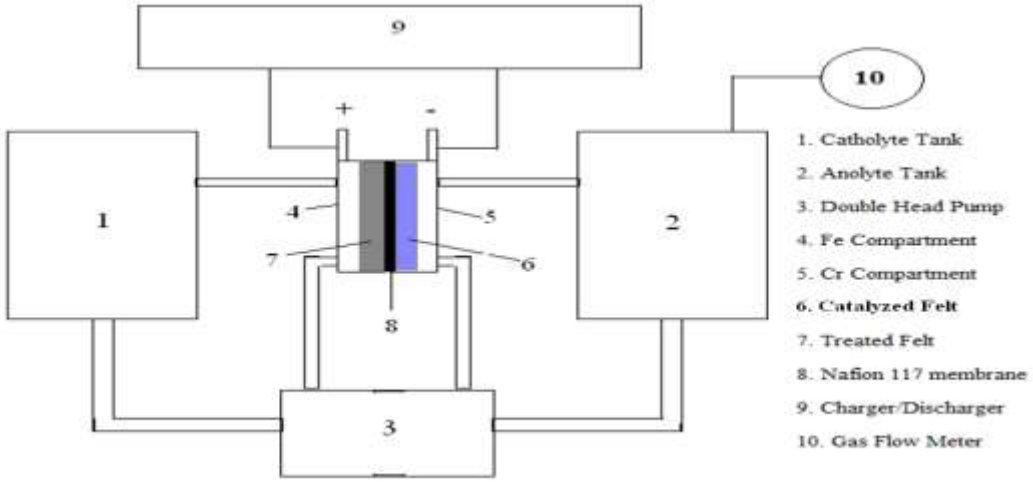

Fig.1. Schematic of redox flow cell setup.

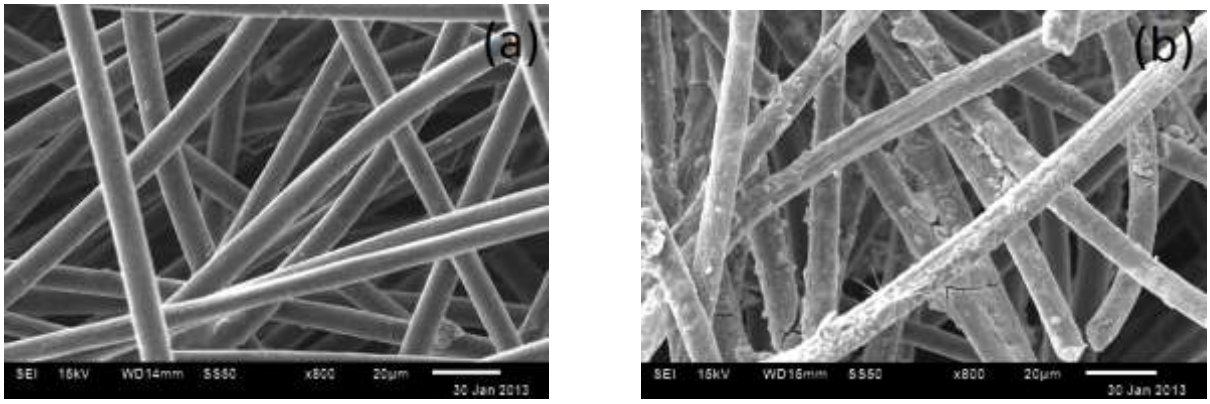

Fig.2. SEM images (a) treated carbon felt and (b) carbon felt plated with Bi-Pb each 8 mg/cm^2.

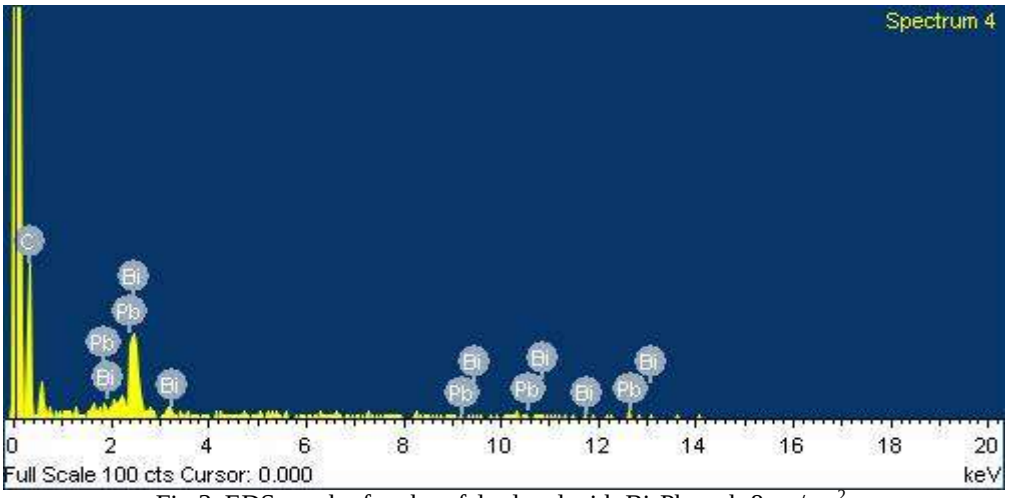

Fig.3. EDS graph of carbon felt plated with Bi-Pb each 8mg/cm^2.

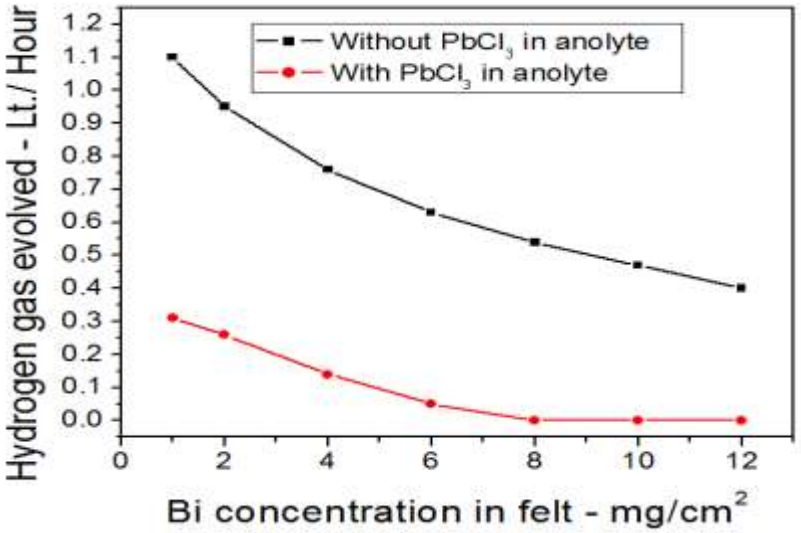

Fig.4. Hydrogen gas evolved with and without 0.01N $PbCl_2$ in anolyte.

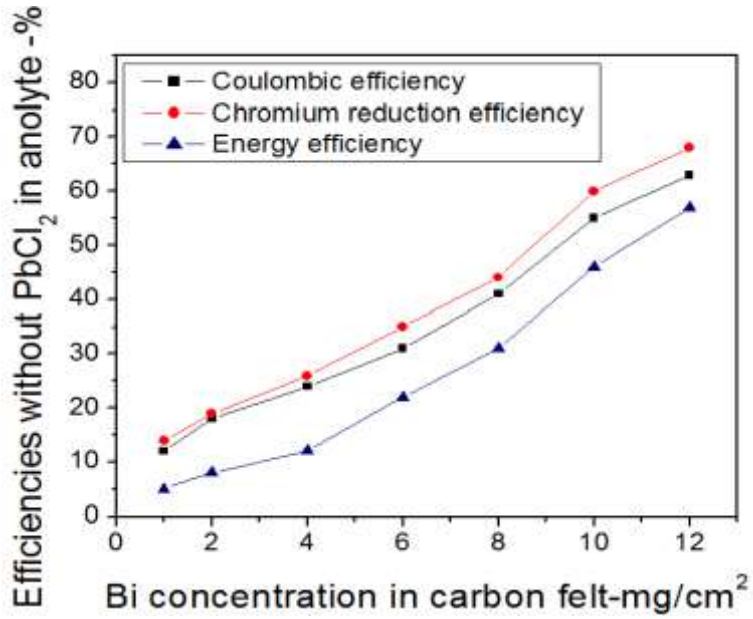

Fig.5. Efficiency values without $PbCl_2$ in anolyte for varying concentration of Bi in carbon felt.

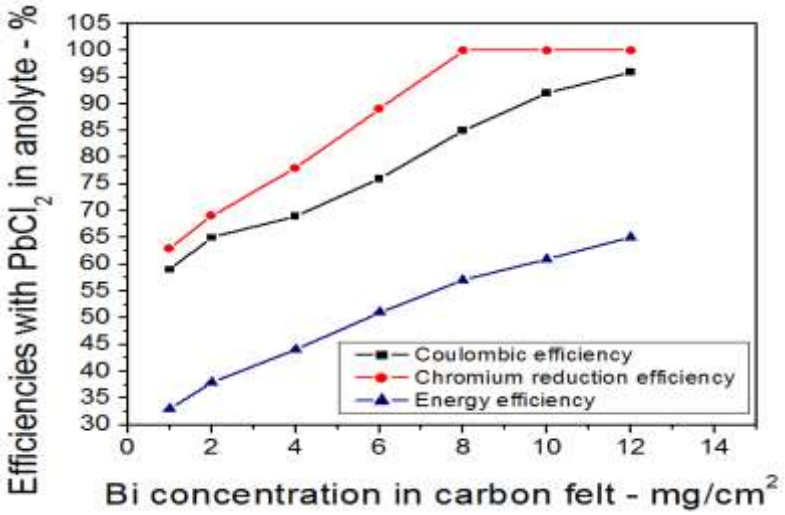

Fig.6. Efficiency values with $PbCl_2$ in anolyte for varying concentration of Bi in carbon felt.

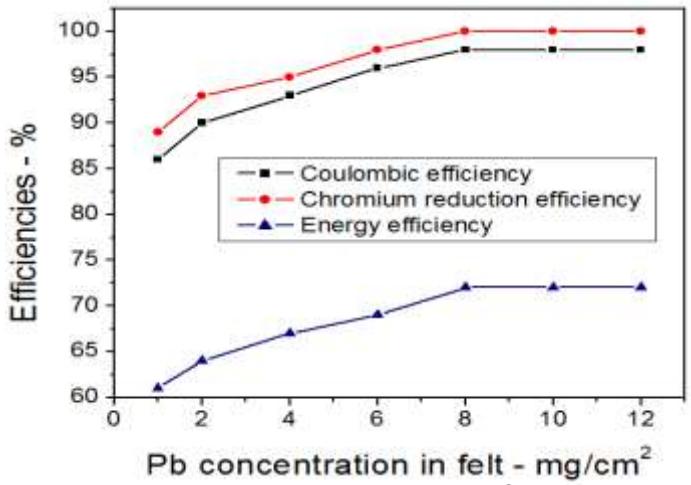

Fig.7. Efficiency values for the electrodes with fixed 8mg/cm^2 Bi and Pb from 1to 10 mg/cm^2.

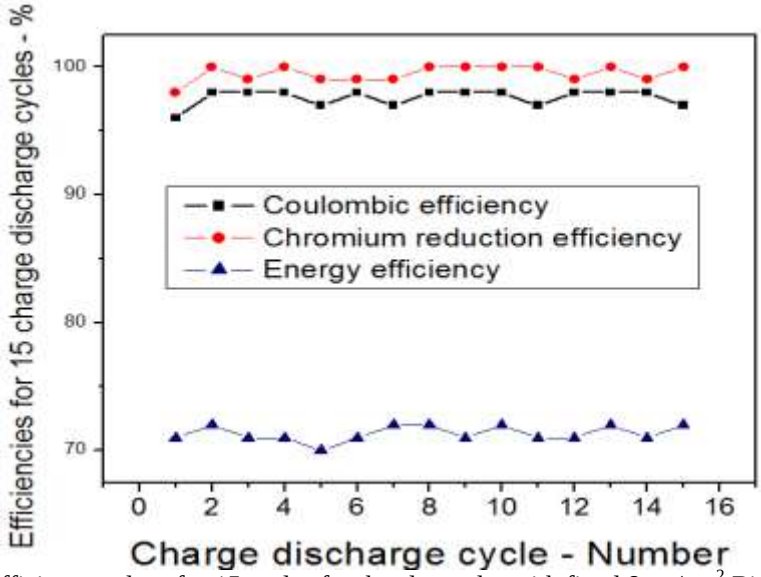

Fig.8. Efficiency values for 15 cycles for the electrodes with fixed 8mg/cm^2 Bi-Pb each.