THINK INDIA JOURNAL

ISSN:0971-1260
Vol-22- Issue-04-October -2019

Synthesis, Characterization And Measurement Of Pb-Bi Electroplating Method For Improvement Of Cr(Iii)/Cr(Ii) Redox In Fe-Cr Redox Flow Cell [1 1]

[1] Prashant Balwantrao Thakare, Dr. Utpal Saha , Dr. Pushpendra Sharma

[1] Research Scholar, Department of Chemistry, Sri Satya Sai University of Technology & Medical Sciences, Sehore.

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 cm2 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

A redox flow battery is an electrochemical energy storage device that converts chemical energy into electrical energy through reversible oxidation and reduction of working fluids. The concept was initially conceived in 1970s. Clean and sustainable energy supplied from renewable sources in future requires efficient, reliable and cost-effective energy storage systems. Due to the flexibility in system design and competence in scaling cost, redox flow batteries are promising in stationary storage of energy from intermittent sources such as solar and wind.

ISSN:0971-1260
Vol-22- Issue-04-October -2019

The question of improving the efficiency of Fe-Cr RFB is directly related to the reversibility of the redox pair Cr(III)/Cr(II). The carbon felt electrode with a low current density of 40 mA / cm^2 was used to achieve this. Several researchers have applied their attempts to improvise the efficiency of redox. As obtained, carbon felt substrates have not been used as electrodes for cell activity. Both need to be pre-treated for standardization in order to achieve strong chemical properties, to catalyze the chromium redox pair. However, the literature has shown that thermodynamic hydrogen has evolved before chromium is reduced. Hydrogen evolution decreases the coulombic efficiency of the system and, over a series of cycles, causes the device to become chemically out of equilibrium, thereby reducing its efficient ability. Pre-cleaning processes for carbon felts were carried out with H_2SO_4, KOH and HNO_3 to achieve good redox properties as well as less hydrogen gas. In addition to normalization procedures, ample anolyte catalysts are needed to improve the redox reaction of chromium and to reduce the hydrogen over its capacity. NASA first proposed au catalytic therapy for carbon felt and the addition of $PbCl_2$ and $BiCl_3$ to anolyte. The combination of Pb, Au, Bi and Tl, thermally impregnated in carbon felts to improve the performance of Fe-Cr RFB has also been studied [1]. Nevertheless, the above-mentioned processes have not attained sufficient coulombic, chromium redox reaction performance and energy efficiency. Maximum coulombic efficiency reported was 97%.

Current study was conducted on electroplated carbon felts with 1-12 mg / cm^2 Bi as a nominee electrode and used on the negative side of the cell with 0.01N $PbCl_2$ as an additive in anolyte. Electrode producing 8mg/cm^2 Bi and 0.01N $PbCl_2$ in anolyte produced significant results. A further research was also performed with a mixture of Bi-Pb electroplated felts to enhance cell efficiency. Bi-Pb hybrid felts were trailed and tested for zero hydrogen gasification, 100% chromium reduction capacity, optimum coulombic and electricity output, so that Fe-Cr redox can be used as a bulk energy storage device for load leveling and stand-alone applications.

II. EXPERIMENTATION

2.1 CHEMICALS AND 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.

ISSN:0971-1260
Vol-22- Issue-04-October -2019

2.2 INSTRUMENTATION USED

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: JSM 6610LV). Concentration of electrolytes was measured by a double beam UV-Vis spectrophotometer.

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 $BiCl_3$ 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.

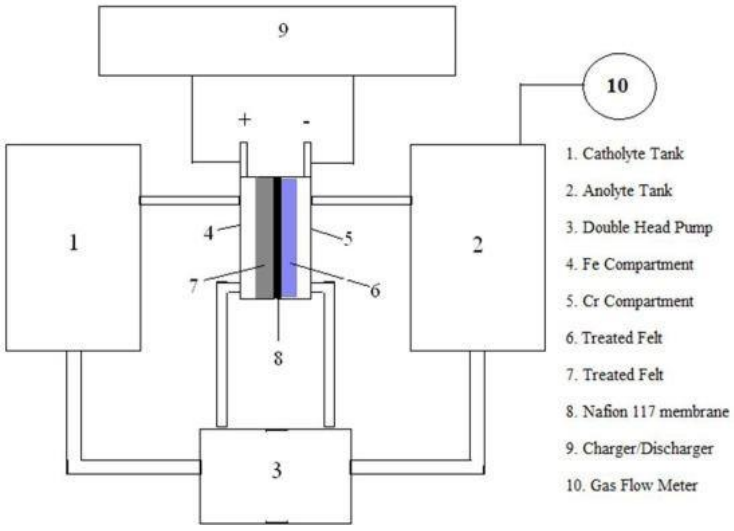

Fig.1: Schematic diagram of redox flow cell setup

III. METHODS

3.1 M ETHODS for pre-treatment of carbon felt

ISSN:0971-1260
Vol-22- Issue-04-October -2019

The carbon felt roll was broken into 100 cm^2 parts which were used as an electrode. Initially as they were provided, carbon felt has high surface tension; thus, it was washed in methanol for 10 minutes, which makes the whole surface area active and usable for cleaning. These cleaned felt was soaked for 48 hours in 40 per cent H_2O_2 to normalize the felt by oxidizing the excess reduction groups in it [2]. Samples were then washed in DI water until pH 7 and dried in a hot air oven at 200°C for 3 hours. Such samples coated with carbon felt were specifically used as electrodes on the positive (Fe) side. Additionally, carbon felting used in the negative side of the cell was catalyzed.

3.2 M ETHOD Pb ELECTROPLATING

$PbCl_2$ was applied to electrolyte as an intermediate in anolyte to catalyze the Cr(III)/Cr(II) redox pair in Fe-Cr RFB to date. In this scientific work, Pb metal was electroplated to carbon felt samples which were used on the negative side of the cell as electrodes.

Many methods were valid for electroplating Pb metal using acidic, simple baths[3], and electro-winning methods [4, 5]. Acidic approaches provide Pb metal with dense and solid plating, while simple baths provide Pb metal with ruff and smooth surface.

But in the current work a method on carbon felt electrode samples was designed and implemented as a fundamental electro-winning method. If an acidic bath employed for the plating of carbon felt the pores are getting blocked by Pb and electrolyte is channelized in flow cell causing short circuit of electrodes and damage to the highly costly Nafion-117 membrane. While a basic bath was used, the plating will not be uniform and uneven surface of Pb plating will be obtained, causing Pb dendrite on electrode surface.

At a maximum density of 10 mA / cm^2 Pb Plating was done. The respective current and time (Ah) information was mentioned in Table-1 in order to get 1 to 12 mg / cm^2 of Pb electroplated felts.

Table-1: 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)
0.5 mg / cm^2	0.05	0.013	01	0.9
1 mg / cm^2	0.10	0.026	1	1.8
2 mg / cm^2	0.20	0.052	1	3.6

ISSN:0971-1260
Vol-22- Issue-04-October -2019

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

3.3 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 $Bi_2(SO_4)_3$ 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. The respective electrical parameters (Ampere-Hour (Ah)) used to achieve 1 to 12 mg / cm^2 Bi electroplated felt have been listed in Table-2 below.

Table-2: 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% [6].

ISSN:0971-1260
Vol-22- Issue-04-October -2019

3.4 M ETHOD OF Bi-Pb ELECTROPLATING

To attain required coulombic and energy efficiencies normalization treatment was required to Carbon felts. Carbon felt roll of 330 mm × 330 mm × 3 mm was cut into samples of 10 cm^2 as per size of required electrode. Such feltings initially had high surface tension as they were received; therefore they were washed in methanol for 10 minutes. M ethanol makes available for cleaning the entire surface by wetting the total active Carbon felt surface area. These washed felts were dipped for 48 hours in 40 per cent H_2O_2 to normalize the feeling by oxidizing the excess reduction groups inside it [2]. The felt samples were washed in DI water until pH al 7 and dried in a hot air oven at 200oC for 3 hours. This felt Caron inert and handled samples were used as electrodes in both sides of the Fe-Cr redox flow chamber.

3.5 NAFION-117 M EM BRANE 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 [7].

3.6 NAFION-117 M EM BRANE 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 were in electrolyte. Upon completion of the cell assessment membranes were soaked as post treatment in 2N HCl to mitigate the fouling effect.

3.7 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 5liter of 1.3M FeCl2 in 2N HCl. The negative electrolyte was 5liter of 1.3M CrCl3in 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

ISSN:0971-1260
Vol-22- Issue-04-October -2019

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.

3.8 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 millimeter.

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. [9].

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

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.

IV. RESULTS & DISCUSS ION

4.1 CHARACTERIZATION OF Bi-Pb CATALYZED CARBON ELTS:

Characterization of Bi-Pb plated samples was also carried out with SEM-EDS system. These samples are prepared by fixing Bi concentration in felt at 8 mg/cm^2, since it has given good

ISSN:0971-1260
Vol-22- Issue-04-October -2019

results individually and Pb content was varied from 1 to 12 mg/cm^2. Fig.2 are SEM images of the plated samples with Bi-Pb.

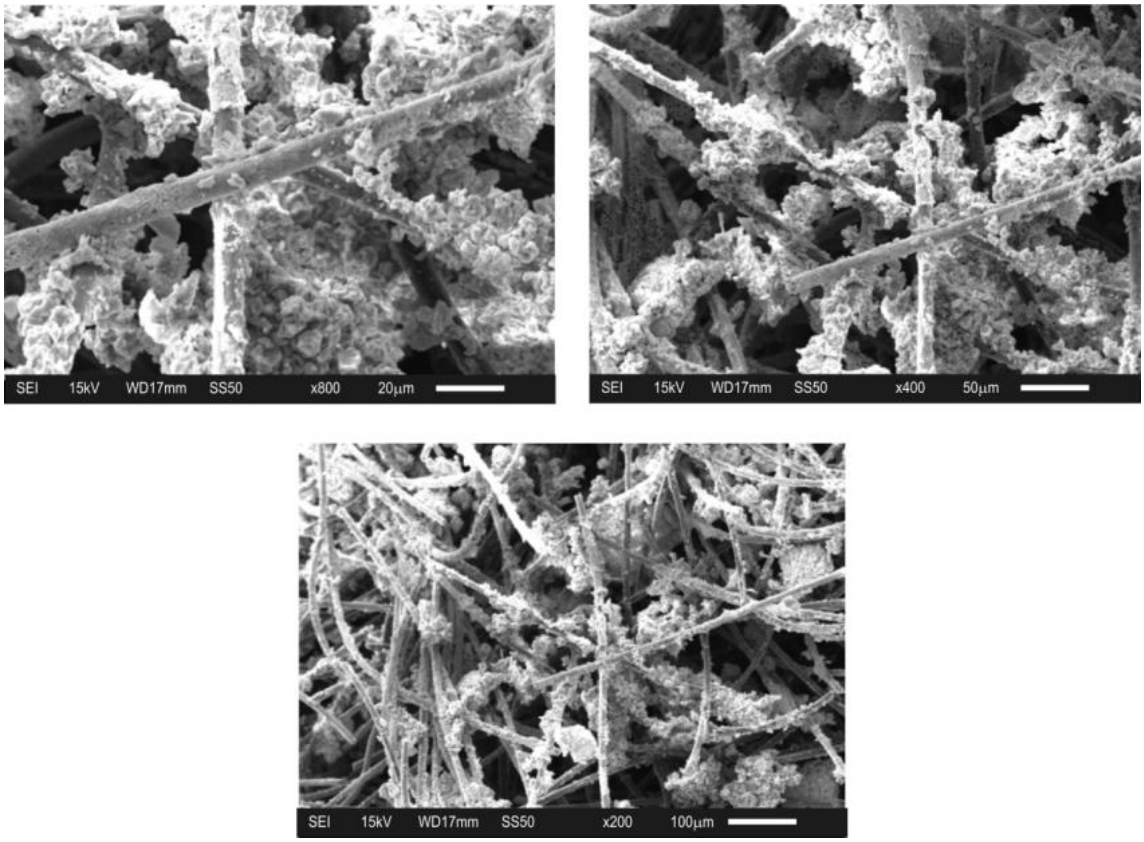

Fig.2 : 12mg/cm^2 Pb on 8 mg/cm^2 plated Bi sample SEM images.

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.

4.2 CHARACTERIZATION OF Bi-Pb CATALYZED FELTS WITH EDS

To confirm the Bi content in felt, EDS analysis was carried out for carbon felt amples which were electroplated with Bi from 1 to 12 mg/cm^2.

The images were shown in Fig.3 were the spectrums which were obtained from the EDS analysis of Bi-Pb catalyzed carbon felts respectively.

ISSN:0971-1260
Vol-22- Issue-04-October -2019

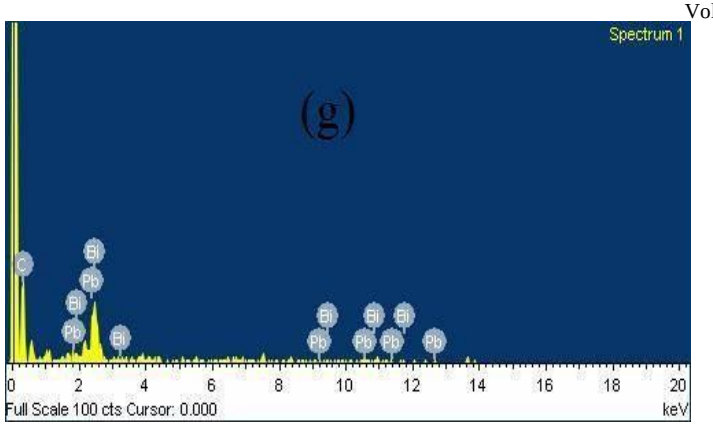

Fig.3: EDS Spectrums of Bi-Pb plated felts

It is confirmed that the EDS spectrums of all the catalyzed carbon felt samples with 1-12 mg/cm^2 Pb on a fixed 8 mg/cm^2 Bi plated carbon felts were shown corresponding and characteristic Bi and Pb peaks. As Pb concentration in samples was increasing the corresponding peaks are also improved till the concentration maxima.

4.3 Pb-Bi PLATED FELTS AS ELECTRODES WITH CHLORIDE ANOLYTE

The performance of the Bi-Pb plated electrodes were investigated for suppression of hydrogen evolution, increase in chromium redox reaction and its single-cell characteristics. Evaluations are carried out by charging of the cell to 100% SOC, with an upper voltage limit of 1.5V and discharging cell, with a lower voltage limit of 0.6V. The cell assessments are carried out at a constant current density of 50 mA / cm^2. An even more study was carried out with the combination of Bi-Pb electroplated felt to improvise the coulombic and energy efficiencies. The felt was prepared by placing the Bi concentration in the felts at 8 mg / cm^2 while the Pb concentration ranged from 1 to 12 mg / cm^2. Increasing coulombic and energy efficiency trends were identified up to Bi 8mg / cm^2 and Pb 8mg / cm^2 concentrations. The influence of Pb concentration in felt was meagre after that. A cumulative reduction of 100% chromium, 98% coulombic and 72% energy efficiency values have been reported. Results were given in Table-3.

ISSN:0971-1260
Vol-22- Issue-04-October -2019

Table-3: Efficiencies for varied Pb content on felt

PbCl2 content on felt mg/cm^2	Coulombic efficiency	Chromium reduction efficiency	Energy Efficiency
1	86	89	61
2	90	93	64
4	93	95	67
6	96	98	69
8	98	100	72
10	98	100	72
12	98	100	72

Results were graphically shown in Fig.4

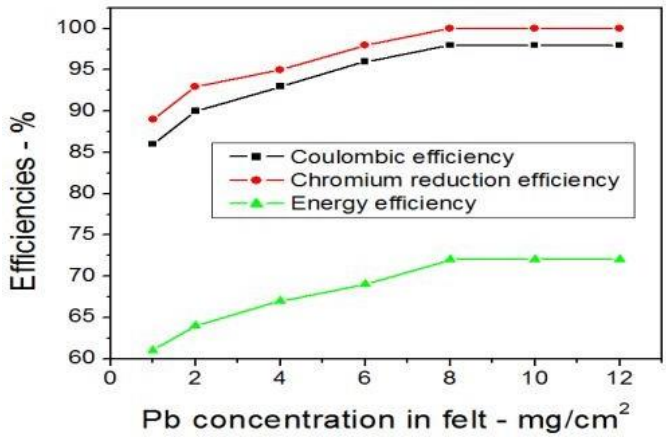

Fig.4: Efficiencies with fixed 8mg/cm^2 Bi, Pb from 1 to 12 mg/cm^2.

To check this performance of the electrode and reproducibility, 15 cycles of charge and discharge and monitoring of the efficiency of chromium reduction, coulombic efficiency, and energy efficiency were conducted. See Table-4 for results. The results showed that the 8mg / cm^2 electrodes of each Bi and Pb carbon felt showed a 98-100 percent reduction in chromium, a 96-98 percent reduction in coulombic efficiencies without evolution of hydrogen gassing and a maximum recorded energy efficiency of 72 percent. Fig.5 revealed these findings.

ISSN:0971-1260
Vol-22- Issue-04-October -2019

Table-4: Efficiencies for 15 Cycles of charge and discharge

Cycle	Coulombic efficiency %	Chromium reduction efficiency %	Energy Efficiency%
1	96	98	71
2	98	100	72
3	98	99	71
4	98	100	71
5	97	99	70
6	98	99	71
7	97	99	72
8	98	100	72
9	98	100	71
10	98	100	72
11	97	100	71
12	98	99	71
13	98	100	72
14	98	99	71
15	97	100	72

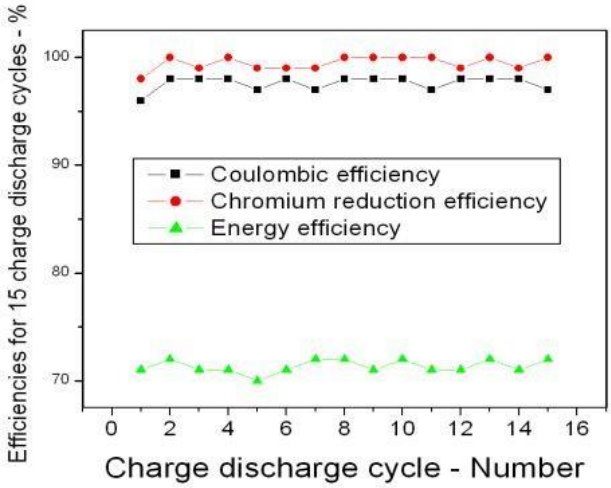

Fig.5: Efficiencies for 15 cycles for the electrodes with fixed 8mg/cm^2 Bi-Pb each.

Bi's reduction potential is more electropositive than Pb and this makes Bi's catalyst component more stable than Pb. Bi oxidizes near the standard potential of chromium, so Bi will not find a solution until the $CrCl_2$ total is converted to $CrCl_3$. For this reason, while Pb tends to deplete at

ISSN:0971-1260
Vol-22- Issue-04-October -2019

low SOC from the electrode, typical cell cycling would not cause Bi to go into solution throughout discharge [7].

4.4 Pb-Bi PLATED FELTS AS ELECTRODES WITH SULPHATE ELECTROLYTES

So far we have developed an optimum condition for better chromium reduction, coulombic efficiency and energy efficiency by using an 8mg each Bi-Pb electroplated carbon felt by using Chloride electrolytes, means active materials were taken as chlorides. A further study was conducted to improvise the coulombic and energy efficiencies using sulphate electrolytes combining Bi-Pb electroplated felt. Ferrous sulphate and chromium sulphate were used as active materials for the cell.

The felts were produced by placing each Bi's concentration at 8 mg / cm^2, while the Pb concentration ranged from 1 to 12 mg / cm^2. Increasing coulombic and energy efficiency trends were observed up to Bi 8mg / cm^2 and Pb 8mg / cm^2 concentrations. The impact of Pb concentration in felt was meagre after that. See Table-5 for details. A maximum efficiency of 100 percent chromium reduction, a coulombic efficiency of 98 percent and energy efficiency values of 78 percent were recorded. Results indicated in Fig.6.

Table-5 : Efficiencies with respect to Pb content in felt

PbCl2 content	Coulombic efficiency %	Chromium reduction	Energy Efficiency%
1	87	93	61
2	91	95	63
4	93	98	70
6	97	98	74
8	98	100	78
10	98	100	78
12	98	100	78

ISSN:0971-1260
Vol-22- Issue-04-October -2019

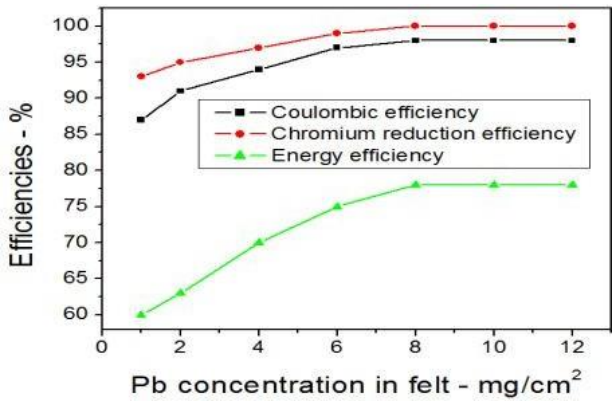

Fig.6: Efficiencies with respect to Pb content in felt

Changing the anolyte color from dark green to satin blue indicates achieving 100 % SOC and 100% reduction in chromium.To test performance of this electrode with sulphate electrolytes and reproducibility of the electrode evaluation was carried out by 20 cycles of charge. Results were given in Table-6.

Table-6: Efficiencies for 20 cycles using Sulphate electrolytes

Cycle	Coulombic efficiency %	Chromium reduction efficiency %	Energy Efficiency%
1	97	98	78
2	98	100	77
3	97	99	77
4	98	100	78
5	97	99	77
6	98	99	77
7	97	99	77
8	98	100	78
9	98	100	78
10	97	99	78
11	97	100	78
12	98	99	77
13	97	100	77
14	98	99	78
15	97	100	78
16	98	100	78
17	98	99	77
18	97	100	78
19	98	100	78
20	98	99	77

ISSN:0971-1260
Vol-22- Issue-04-October -2019

Monitoring of the efficiency of chromium reduction, coulombic efficiency and energy efficiency of the 8mg / cm^2 Bi and Pb carbon felt electrodes showed 98-100% DCr, 96-98% DC and 78% DE. The results represented graphically in Fig.7.

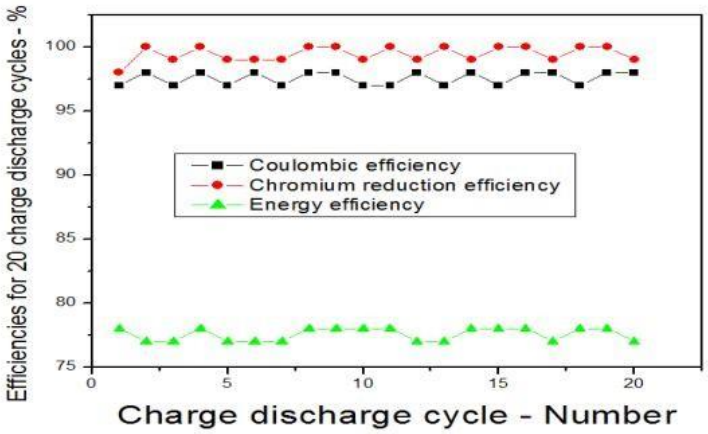

Fig.7: Efficiencies for 20 cycles of charge and discharge

The improvement in efficiencies can be clarified on the basis of Bi's reduction potential, which is more electropositive than Pb, which allows the catalyst part Bi more robust than Pb. Bi oxidizes past the normal potential of the chromium-electrode[11]. Even though the cell was kept ideally, Bi and Pb will not go into anolyte because of using sulphate electrolytes. As a result of these electroplated carbon felts with Bi-Pb achieved efficiencies are better than previous works performed on the same Fe-Cr redox flow cell [10,12]

V. CONCLUSIONS

The method of plate Bi metal to carbon felt was completely satisfactory at a temperature of 100°C. The method applied to the plate Pb metal to carbon felt was completely satisfactory at pH 11 at room temperature (32°C). Achieved 100% Chromium Reduction Efficiency, 98% Coulombic Efficiency and 72% Energy Efficiency for Fe-Cr Redox Flow Cell with 8 mg / cm^2 Bi-Pb material each. It is verified that H_2O_2 treated carbon felt with Bi-Pb up to 8 mg / cm^2 is a functional electrode on the negative side of the Fe-Cr redox flow cell at room temperature (32°C) so that electrolyte heating is not necessary. The catalyzed felts were used for single cell measurements with an electrode area of 100 cm^2 at a current density of 50 mA / cm^2.

REFERENCES

1. Cathro KJ, Cedzynska K, Constable DC (1987) J Power Sources19:337

2. Lopez-Atalaya M, Codina G, Perez J.R, Vazquez J.L, Aldaz A. Journal of Power Sources,

ISSN:0971-1260
Vol-22- Issue-04-October -2019

39 (1992) 147-154.

3. M. Joerdan “Electrodeposition of Tin–Lead Alloys”, in Modern Electroplating, Fifth Edition (eds M. Schlesinger and M. Paunovic), John Wiley & Sons, Inc.
4. R. D. Prengaman, H. B. Mc Donald, US Patent 4229271(1980)
5. T. Bieszczad, S. Sanak-Rydlewska, Physicochemical Problems of Mineral Processing, 35(2001),181.
6. V. Baltazar and L. C. Jhon, US patent 5378328, 1995.
7. Perez J.R, Lopez-Atalaya M, Codina G, Vazquez J.L, Aldaz A. Bull. Electrochem. 1991, 7, 555-558
8. R. A. Assink, J. Membr. Sci. 1984, 17, 205–217.
9. http://en.wikipedia.org/wiki/Ampere-hour, <Date visited Feb 27, 2013>
10. groups/gpnm/graphite-products-for-redox-flow-batteries/material.Jalan V, Stark H, Giner J. NASA CR-165218, DOE/NASA/0097-80/1, 1981.
11. NASA Technical report. NASA TM-83087, DOE/NASA/12726-19, 1981.
12. C. P. de-Leon, A. F. Ferrer, J. G. Garcia , D.A. Szanto and F.C. Walsh, Redox flow cells for energy conversion, Journal of Power Sources 160 (2006) 716-732.