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Synthesis, Characterization and Evaluation of Pb Electroplated Carbon felts for Achieving Maximum Efficiency of Fe-Cr Redox Flow Cell

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Abstract: *To catalyze Cr(III)/Cr(II) redox couple, Pb was used as candidate catalysts. Pb has a remarkable behavior on reduction and oxidation of chromium couple to enhance the performance of Fe-Cr redox flow cell. In the present investigation catalyzed carbon felt substrates were used as electrodes on negative side which were electrochemically plated/ loaded with Pb from 0.05g to 1.2g. The cell comprising 0.8 g Pb loaded felt has shown 100% Chromium reduction efficiency, 98% coulombic efficiency and zero hydrogen gassing at 32°C for 15 cycles of charge and discharge. 5liters of 1.3N $FeCl_2$ in 2N HCl as catholyte, 1.3N $CrCl_3$ in 2N HCl as anolyte containing 0.05N $BiCl_3$ as additive were used as electrolytes. The cell operated with Nafion-117 PFSA membrane. 100 cm^2 GFA grade carbon felts with 3mm thickness were utilized as electrodes at a current density of 50 mA/ cm^2.*

Keywords: Fe-Cr redox flow cell; Pb electroplated felts; $BiCl_3$ as additive; Chromium reduction efficiency; Coulombic efficiency

1. INTRODUCTION

In the 1970s NASA studied the Redox Flow Battery (RFB) for building stationary energy storage systems. The cells of RFB's are easily stacked in parallel or series for increasing the power or voltage output. By increasing the volume of the electrolytes in external storage tanks energy capacity can be scaled up to 10MW makes RFB's attractive candidates for large stationary storage applications [1-6]. Fe-Cr RFB works on redox couples Fe^{2+}/Fe^{3+} and Cr^{3+}/Cr^{2+} as positive and negative respectively. Both the electrolytes are acidified with 2N HCl solution.

Due to this feature Fe-Cr Redox system was first studied by NASA and many other researchers were added their efforts to optimize the performance. Slow kinetics of Cr(III)/Cr(II) was observed by the presence of Cr(III) aqua and chloro complexes such as $Cr(H_2O)_6^{3+}$ and $Cr(H_2O)_6Cl^{2+}$ [7-11].

Fe-Cr redox flow cell performance is significantly affected by the pretreatment and catalytic characteristics of the carbon felts [12]. However, the literature shown that thermodynamically hydrogen has been 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. Normalization treatments were performed on carbon felts for attaining good chemical properties, improving redox reaction of chromium and to decrease the hydrogen over potential. 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 [13-14]. In addition to normalization treatments sufficient catalysts are needed in anolyte to improve the redox reaction of Chromium. Au catalytic treatment and addition of Pb and Bi in electrolyte was first suggested by NASA [15-16]. Combination of Pb, Au, Bi and Tl metals were thermally impregnated in carbon felts to improve the performance of Fe-Cr RFB [17]. But considerable coulombic and chromium redox reaction efficiencies were not achieved by the above processes.

In the present work Pb electroplated carbon felts ware prepared as candidate electrodes for negative side of the cell. A combination study of with and without $BiCl_3$ as additive in anolyte was also carried out to improve the performance of the cell and to achieve 100% chromium reduction efficiency, zero hydrogen gassing and maximum coulombic efficiency, so that Fe-Cr RFB can be used as a bulk energy storage system for load leveling & stand-alone applications.

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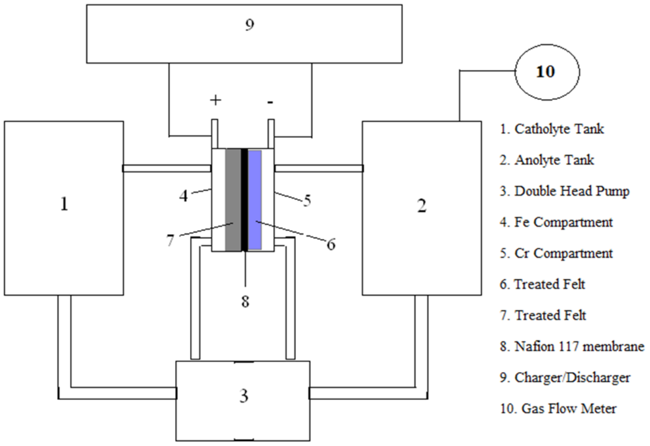

Figure 1. Fe-Cr redox flow cell setup.

2. EXPERIMENTATION

2.1. Materials & Reagents

Carbon felt (Nominal thickness 3 mm, Bulk density 0.1 g/cm^3, Area weight 300 g/m^2, Electrical resistivity: through plane < 15 Ω.mm and in plane < 5 Ω.mm , GFA Grade, M/s SGL carbon, Germany [18]), Graphite Moulds, Nafion-117 PFSA Membrane (Dupont, USA), KCl, K_2CO_3, CH_3OH, 40% H_2O_2, HCl, $FeCl_2.6H_2O$, $CrCl_3.6H_2O$, Pb (Metal sheet), Pb $(CH_3COO)_2$, 30% NH_3 solution, CH3COONH$_4$, $BiCl_3$ and DI Water.

2.2. Instrumentation

Evaluation of Pb uniform dispersion and amount of Pb plated on carbon felt was determined by Scanning Electron Microscope (SEM)- Energy Dispersive Spectra (EDS) Instrument (Make: JEOL, Model No: JSM6610LV). Concentration of electrolytes was done by double beam UV-Vis spectrophotometer (Make: Systronics, Model No: 2201) [19].

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 $CrCl_3$, 0.05N $BiCl_3$in 2N HCl. Both the electrolytes pass through the respective chambers (4) and (5) made up of graphite called as moulds. The treated and catalyzed 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 by using a gas flow meter (10) (Toshniwal).

2.4. Procedure

2.4.1. Procedure for preparation of treated and catalyzed felts

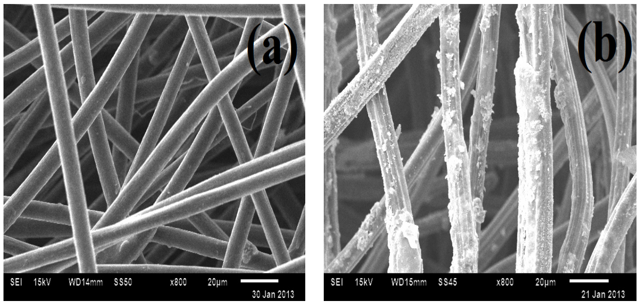

Figure 2. SEM images: (a) H_2O_2 Treated carbon felt and (b) 0.8g Pb loaded electrode and (c) Pb crystallite size magnified image.

The roll of the carbon felt actually available size is 330X330X3 mm. It was divided into 100 cm^2 pieces which was size of electrodes for all evaluations. Carbon felts posse's high surface tension initially as they were received; hence they were cleaned in methanol for 10 minutes, which makes the entire active surface area 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 [20]. Then felt samples were washed in DI water until the pH≈7 and dried at 200°C for 3 hours in a hot air oven. These treated carbon felt samples were used as electrodes on positive (Fe) side directly.

Additional to H_2O_2 treatment electrode samples which were used in negative (Cr) side of the RFB were plated with Pb up to 12 mg/cm^2. For electroplating of Pb several methods were available using acidic baths, basic baths [21], using electro-winning methods [22-23]. But in present experimental study, 400g of lead acetate and 400g of ammonium acetate were dissolved in one liter of DI water taken as bath for plating. Treated carbon felt samples were initially dipped in 30% ammonia solution for 2 minutes and placed in bath. Pb metal sheets were utilized as anodes and felts were applied to a negative charge. Soluble Pb metal sheets were used as anodes to keep bath free of PbO_2. Plating was carried out at a current density of 10 mA / cm^2. To get 0.5 to 12 mg/cm^2 Pb electroplated felts, the respective current and time (Ampere-Hour (Ah)) information was mentioned in Table 1. The value of time in minutes was corrected according to coulombic efficiency of the process

Table 1. Optimization of electrical parameters given to produce catalyzed felts

Catalyzed Pb electrode sample of 100 cm^2	Required Pb (g)	Required Ah to electroplate Pb	Ampere to put (A)	Required time for plating (min)
0.5 mg/cm^2	0.05	0.013	1	0.9
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

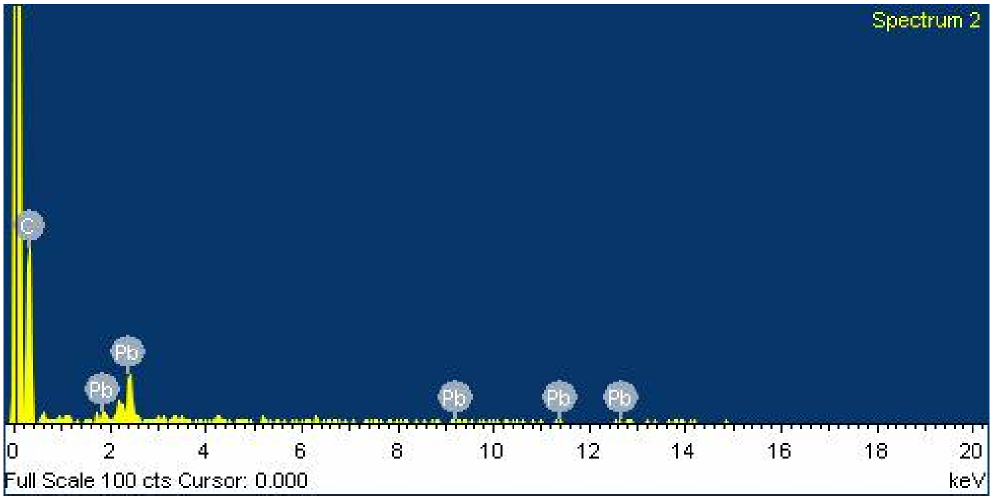

Figure 3. EDS graph of 0.8g Pb loaded electrode.

(92%). By using 30% ammonia solution bath pH was maintained at 11 throughout the plating experimentation. Because of the basic bath procedure, Pb was plated to carbon felts not affected the porosity of the carbon felts.

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

In the present research work Nafion-117 PFSA was used as Proton Exchange Membrane (PEM), it can reduce the cross contamination of the Fe and Cr [20, 24, 25]. The rate of transfer of H^+ ions proportional to current density maintained on electrodes. 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 [25]. After completion of cell evaluation membranes were soaked in 2N HCl as post treatment process to minimize the fouling effect.

2.4.3. Procedure for cell assembly

During the cell assembly Pb electroplated felts were used as electrodes on Cr side and H_2O_2 treated felts were used as electrodes on Fe side. H_2O_2 treated and Pb loaded felts were placed separately in graphite moulds, in between them the Nafion-117 membrane was arranged by the help of gaskets. Moulds were tightened with sleeved screws and the cell was then placed in test setup. 250 ml/min uniform flow rate for both the electrolytes was maintained for all the cell evaluations.

2.4.4. Procedure for cell evaluation

The Fe-Cr redox flow cell works with an anolyte and catholyte, both the electrolytes are prepared with 1.3N active materials by dissolving $CrCl_3$ and $FeCl_2$ in 2N HCl respectively. These electrolytes are pumped in to respective compartments (moulds), by using double headed pump. Constant current was supplied and discharged through these electrodes using the terminals of the graphite moulds. Electrodes pick the charge and convert the active materials as charged and discharged species by transferring protons through membrane. 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.

During charge at positive electrode ferrous ions were converted to ferric ions and at negative electrode chromic ions were converted into chromous ions

$Fe^{2+} - e^- \rightarrow Fe^{3+}$ (charge)

Which shows +0.77V versus Standard Hydrogen Electrode (SHE)

$Cr^{3+} + e^- \rightarrow Cr^{2+}$ (charge)

Which shows −0.41V versus SHE

While discharge at positive electrode ferric ions were changed to ferrous ions and at negative electrode chromous ions were changed into chromic ions

$Fe^{3+} + e^- \rightarrow Fe^{2+}$ (discharge)

Which shows -0.77V versus SHE

$Cr^{2+} \rightarrow Cr^{3+} + e^-$ (discharge)

Which shows +0.41V versus SHE

Open Circuit Voltage (OCV) will be net of the two voltages versus SHE that is

$0.77V - (-0.41V) = 0.77V + 0.41V = 1.18V$

3. RESULTS AND DISCUSSION

3.1. Characterization of Electrodes

The electrochemical loading of Pb on carbon felts was carried out from 0.05g to 1.2g on a 100 cm^2 electrode. To determine the uniform dispersion of the Pb in carbon felts, samples were examined by SEM. The magnified SEM images of non plated, Pb loaded electrode which was 0.8g in 100cm^2 were shown in Fig.2. Uniform dispersion of Pb content on carbon felt was observed. Pb loaded carbon fibers are having an average size of 1.38 microns while; non-plated carbon fibers are having an average size of 1.25 microns. Pb will not posses any morphology, there is no conversion of Pb to PbO_2 on carbon felt, which can be observed by EDS image shown in Fig.3.

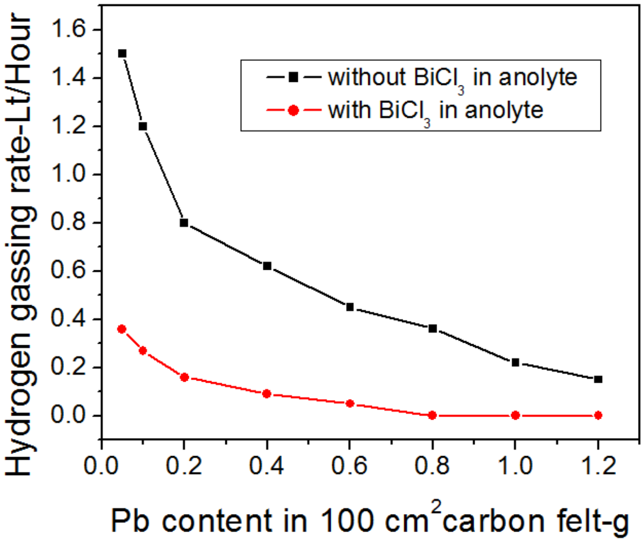

Figure 4. H_2 gas evolution with and without $BiCl_3$ additive in anolyte.

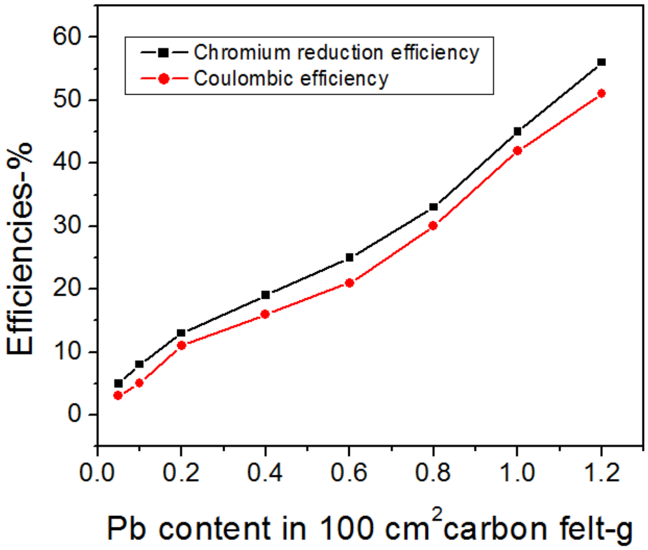

Figure 5. Efficiencies without $BiCl_3$ in anolyte.

3.2. Evaluation of electrodes

The performance of the electrodes prepared by above method has been investigated basing on suppression of hydrogen evolution, chromium redox reaction and its single-cell characteristics. Evaluations are based on charging of the cell to 100% SOC, with an upper voltage limit of 1.5V and discharging cell, with a lower voltage limit of 0.7V. Cell evaluations are done at a constant current density of 50 mA/ cm^2.

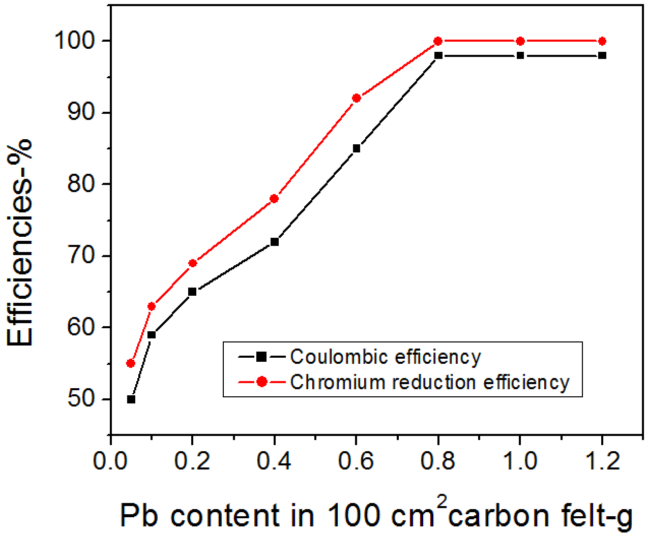

Figure 6. Efficiencies with $BiCl_3$ in anolyte.

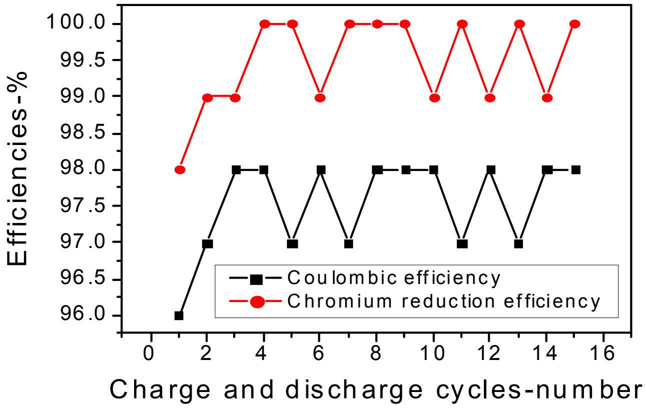

Figure 7. Efficiencies recorded in 15 cycles for 0.8g Pb loaded felt with 0.05N $BiCl_3$ in anolyte.

To suppress the hydrogen gas evolution and to know the required practical catalytic concentration of Pb, the cell evaluations were carried out without $BiCl_3$ in anolyte initially. Hydrogen gas suppression was observed with respect to the concentration of Pb in felt, Even though, the cell evolved 0.2Lt./hour hydrogen gas which is using 12mg/cm^2 Pb catalyzed felt. Further experiments were carried out with 0.05N $BiCl_3$ in anolyte. The combination resulted less hydrogen gassing starting with 0.5 mg/cm^2 felt and no hydrogen gas was evolved after the Pb concentration reached to 8mg/cm^2. Results of hydrogen evolution with 0.5 to 12 mg/cm^2 electrodes with and without the additive $BiCl_3$ 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 $BiCl_3$ in anolyte. Without $BiCl_3$ in anolyte a maximum of 57% chromium reduction and 51% coulombic efficiencies were recorded. While the experiments with 0.05N $BiCl_3$ in anolyte were observed 100% chromium reduction efficiency and 98% coulombic efficiency when the Pb concentration in the carbon felt was 0.8g. Increasing trend of chromium reduction efficiency and coulombic efficiency was observed up to the Pb concentration in electrode was 0.8g after that the effect was mea-

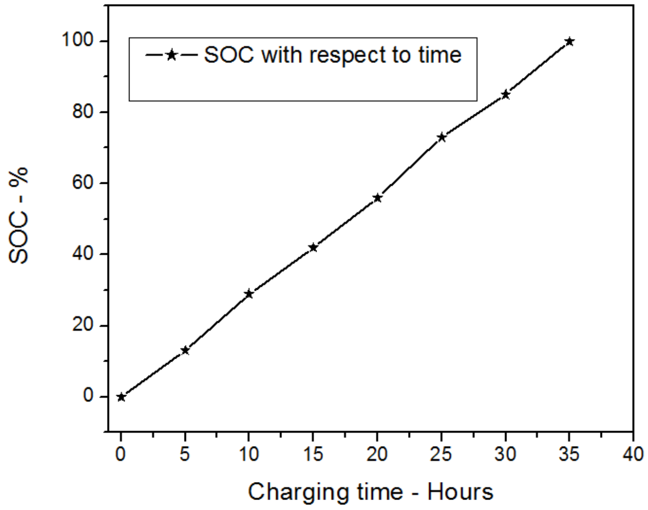

Figure 8. SOC of the cell with respect to charging time.

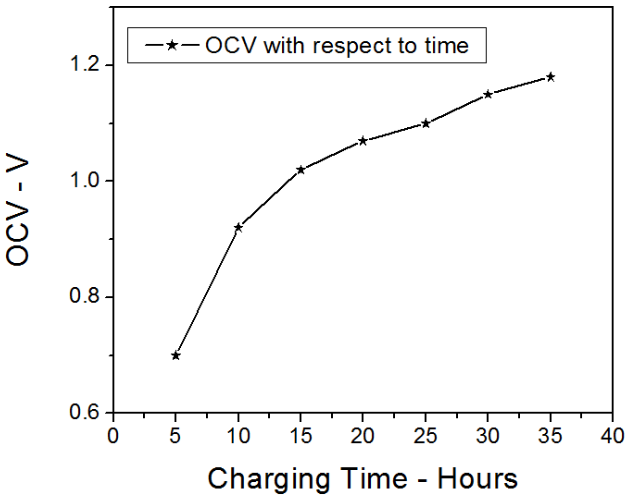

Figure 9. OCV of the cell with respect to charging time.

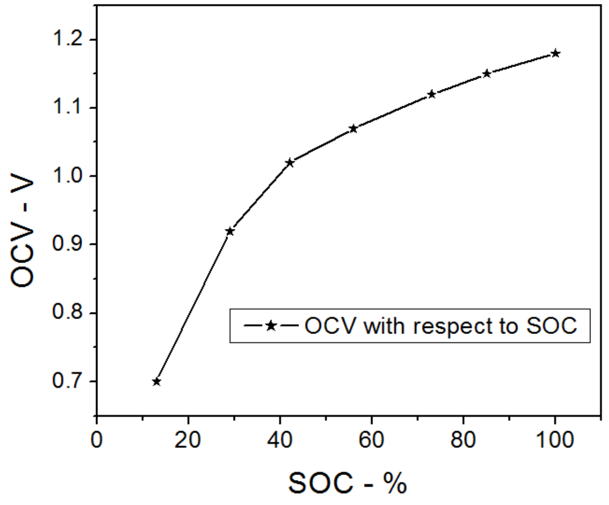

Figure 10. OCV of the cell with respect to SOC.

ger. The experimental results were shown in Fig.5 were without 0.05N $BiCl_3$ in anolyte and for the evaluation of the cell with 0.05N $BiCl_3$ additive in anolyte were shown in Fig.6.

A further study was carried out to evaluate electrodes performance and reproducibility by conducting 15 cycles of charge and discharge, when the Pb content in the carbon felt was 0.8g and $BiCl_3$ concentration was 0.05N in anolyte. Based on results of 15 cycles of charge and discharge, it is observed that 98-100% chromium reduction efficiency, 96-98% coulombic efficiency was observed without hydrogen gassing evolution. These results were shown in Fig.7.

Plots of SOC and OCV with respect to time for the cell evaluations were given in Fig.8 and Fig.9 respectively. A plot of OCV with respect to SOC was given in Fig.10.

This increasing trend of coulombic efficiency and chromium reduction efficiencies can be explained based on the surface catalytic properties of Pb, which acts as an electron mediator from electrode to the chromium. Bi metal is having ability to form chloro-complexes with chloride ion in solution phase as $[BiCl_4]^-$, $[BiCl_5]^{2-}$ and $[BiCl_6]^{3-}$ to stabilize the $CrCl_2$ formed in the solution, while charging of the cell [26].

The redox flow cell has achieved better performances compared to previous research work. The cell efficiencies are obtained by using Nafion-117 membrane, which is having high selectivity for ion transfer so that resistance of the cell was high when compared to other membranes. A comparison of present research work with other literature was given in Table 2.

4. CONCLUSIONS

1. The methodology applied to load Pb metal on carbon felts with present method was entirely satisfactory at pH 11 and at 32°C.
2. Achieved 100% chromium reduction efficiency and 98% coulombic efficiency and 68% energy efficiency for the Fe-Cr redox flow cell with 0.8g Pb loading on carbon felts and with 0.05N $BiCl_3$ as additive in anolyte.
3. It is confirmed that H_2O_2 treated carbon felt possessing Pb up to 0.8g on a 100cm2 electrode area is practical electrode for the negative side of the Fe-Cr redox flow cell at 32°C for 1:1 propagation of the reaction, so that heating of the electrolytes was not required.
4. 0.05N $BiCl_3$ as additive in anolyte induced a high chromium

Table 2. Comparison of cell performances with other literature

Reference	Work output	Present Work output
[8]	Max of 73mW/cm^2 discharge power density with mixed reactant mode	Max of 65mW/cm^2 discharge power density with separated reactant mode
[15, 16, 17]	Combination of Au, Bi, Pb and Tl metals are required to achieve sufficient catalysis	Only Pb loading up to 0.8g on a 100cm2 carbon felt and 0.05N BiCl3 in anolyte was required to sufficient catalysis.
[28, 29]	Heating of electrolytes to 60°C	Catalysis happens at 32°C
[9, 30]	Catalysis was affected by Cr^{3+} aqua and chloro complexes	Catalysis was achieved to attain 1:1 propagation of the Cr(III)/Cr (II) reaction

reduction efficiency and coulombic efficiency.

5. The catalyzed felts were utilized for the single cell evaluations with an electrode area of 100 cm^2 at a current density of 50mA/cm^2.

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