



Investigation of Hydroxylated Carbon Felt Electrode in Vanadium Redox Flow Battery by Using Optimized Supporting Electrolyte

Mohammad Zarei-Jelyani*, Mohsen babaiee, Abdolmajid Ghasemi, Rahim Eqra

Institute of Mechanics, Iranian Space Research Center, Shiraz, Iran
P A P E R I N F O
Paper history:

Received 15 February 2017

Accepted in revised form 16 August 2017

Keywords:

Vanadium redox flow battery

Carbon felt

Hydroxylation

Supporting electrolyte

Wettability

A B S T R A C T

Traditional vanadium batteries use pure sulfuric acid as electrolyte, but H₂SO₄ does not absorb enough vanadium ions to make the electrolyte an efficient energy source. This study investigates the effect of hydroxylation process on electrochemical and operational properties of carbon felt electrode in VOSO₄ solution with an optimized supporting electrolyte (a mixture of six parts HCl and 2.5 parts H₂SO₄). Carbon felt electrode was hydroxylated with mixed acids of H₂SO₄ and HNO₃ in a stainless steel autoclave for 6 h. Then thermal treatment of electrode was performed at 400°C for 5h. Obtained results of cyclic voltammograms showed that when the carbon felt was hydroxylated, both oxidation and reduction peak currents were increased remarkably and the peak potential separation is decreased from 356 to 246 mV, suggesting that the electrochemical activity and the kinetic reversibility of hydroxylated carbon felt electrode were improved compared to the pristine one. According to results of electrochemical impedance spectra, charge transfer resistance (R_{ct}) was calculated to be 648 Ω for pristine carbon felt. The obtained R_{ct} at hydroxylated electrode (176 Ω) shows a decrease of about 73 % in R_{ct}. Charge-discharge profiles of two cells assembled with the pristine carbon felt (cell A), and hydroxylated carbon felt (cell B) showed that energy, voltage and coulombic efficiencies were significantly improved by using the hydroxylated electrodes inside the cell of vanadium redox flow battery.

1. INTRODUCTION

Redox flow battery (RFB) is an electrochemical energy storage device, whereby the electro-active species are stored externally and these reactants are circulated through cell-stack as required [1]. RFB system is considered to be ideal for large scale energy storage, due to its advanced characteristics such as high energy conversion efficiency, high reliability, long cycle life, flexible design, fast response, and low operation and maintenance costs [2-4].

Among various kinds of RFB, all vanadium redox flow battery (VRFB) is a promising and the most developed one, which employs V(II)/V(III) and V(IV)/V(V) as the negative and positive redox couples, respectively[5].

The electrode as one of the key parts of the battery provides active sites for the redox reactions, so an ideal electrode should possess high electrical conductivity, stability in the concentrated acid solution and high electrochemical activity. To date, carbon based

materials such as carbon felt and carbon paper have been widely used as electrode substrates because of their large surface area and corrosion resistance in the acid solution [6, 7].

However, the pristine carbon materials still show poor kinetic reversibility [6]. Considerable studies on the modification of the electrode materials have been carried out to enhance their electrochemical performance, those methods include ion exchange, heat or acid treatment [8-10], electrochemical oxidation [11], metal deposition [12], etc.

B.Sun et al. showed that the surface functional groups of C-O-H and C=O of graphite felt increased dramatically after thermal and acid hydroxylation, and it was found that great improvement of energy efficiency of vanadium redox cell was obtained after thermal treating at 400°C or treating with boiling concentrated sulphuric acid [8, 9].

However, traditional vanadium batteries use pure sulfuric acid as electrolyte, but H₂SO₄ does not absorb enough vanadium ions to make the electrolyte an efficient energy source. In addition, H₂SO₄ limits the battery's working temperature range to 10-40°C, because VOSO₄ crystallize below this range and V₂O₅

*Corresponding Author's Email: zjmohammad.ui@gmail.com (M. Zarei-Jelyani)

precipitates out above it, rendering the battery useless. Researchers at the U.S. Dept. of Energy's (DOE) Pacific Northwest National Laboratory (PNNL) tested several electrolytes to replace the pure sulfuric acid. They showed that the optimized formula is a mixture of six part HCl and 2.5 parts H₂SO₄ [13]. Yue et al. hydroxylated carbon papers with a mixture containing H₂SO₄ and HNO₃ ($\frac{V_{H_2SO_4}}{V_{HNO_3}} = \frac{3}{1}$) to be used as electrodes of vanadium redox flow battery [14]. However, Yue et al. only used hydroxylation process to modify their electrodes, and their supporting electrolyte was only H₂SO₄. However, so far, there is no direct study about combination of hydroxylation and thermal treatment of carbon felt electrode in VRFB that uses optimized mixture of supporting electrolyte (i.e. six part HCl and 2.5 parts H₂SO₄). In this study, a mixture containing sulfuric and nitric acid was used to hydroxylate the carbon felt electrode in a stainless steel autoclave. Then the electrode was thermal treated in the furnace. The cyclic voltammetry and electrochemical impedance spectroscopy studies of pristine carbon felt (PCF) and hydroxylated carbon felt (HCF) electrodes were performed in VOSO₄ solution with optimized mixture of HCl and H₂SO₄ as supporting electrolyte. In addition, a vanadium battery cell was designed and fabricated in which optimized electrolyte was used in order to evaluate the operational parameters of PCF and HCF electrodes in vanadium redox battery.

2. EXPERIMENTAL

A sample of carbon felt electrode with a thickness of 10 mm was hydroxylated with mixed acids of H₂SO₄ and HNO₃ ($\frac{V_{H_2SO_4}}{V_{HNO_3}} = \frac{3}{1}$) in a stainless steel autoclave at 120°C for 6 h. In order to stabilize the hydroxylated electrode, thermal treatment was performed at 400 °C [8] for 5h.

In order to assess the ability of carbon felt electrodes to absorb optimized VOSO₄ electrolyte, PCF and HCF electrodes (in dimensions of 1 cm × 1cm) were washed in distilled water and then dried at 90 °C. The dry weight of each electrode was measured. Then the electrodes were immersed in solution of 0.2 M VOSO₄ with supporting electrolyte of 0.5 M H₂SO₄ and 1.2 M HCl for twenty seconds and then removed from the solution. When no water drop was dripping, the wet weight of the PCF and HCF electrodes were measured. The electrochemical impedance spectroscopy studies were performed in the solution of 0.2 M VOSO₄ and 0.2 M V₂O₅ in supporting electrolyte of 0.5 M H₂SO₄ and 1.2 M HCl (2.5 parts H₂SO₄ and 6 parts HCl). Also the cyclic voltammetry measurements were done in a solution of 0.2 M VOSO₄ with (0.5 M H₂SO₄ + 1.2 M HCl) supporting electrolyte. A three-electrode system was used with carbon felt as working electrode, an

Ag/AgCl electrode as the reference electrode, and a platinum electrode as the counter electrode in order to evaluate the electrochemical characteristics of PCF and HCF electrodes. The cyclic voltammogram measurements were carried out by using potentiostat and galvanostat devices (Autolab PGSTAT204, NOVA software) at a scan rate of 5.0 mV.s⁻¹. The faradaic impedance spectrum was recorded by applying a bias potential equal to the open circuit voltage (OCV). The applying AC voltage was 10 mV in amplitude in the frequency range of 100 mHz to 10 kHz. The experimental Nyquist plots were simulated using an equivalent electronic circuit. For this purpose, the fit and the simulation options in the frequency response analyzer (FRA) of the NOVA software were employed. In order to study the effect of carbon felt hydroxylation on the VRFB operation, a VRFB cell was designed and fabricated using an electrolyte of 1 M VOSO₄ in the optimized supporting electrolyte of 6 M HCl and 2.5 M H₂SO₄. The entire processes of design, fabrication, assembly and sealing of this VRFB cell were conducted at Institute of Mechanics, Iranian Space Research Center. Fig. 1 shows laboratory unit of fabricated VRFB cell.

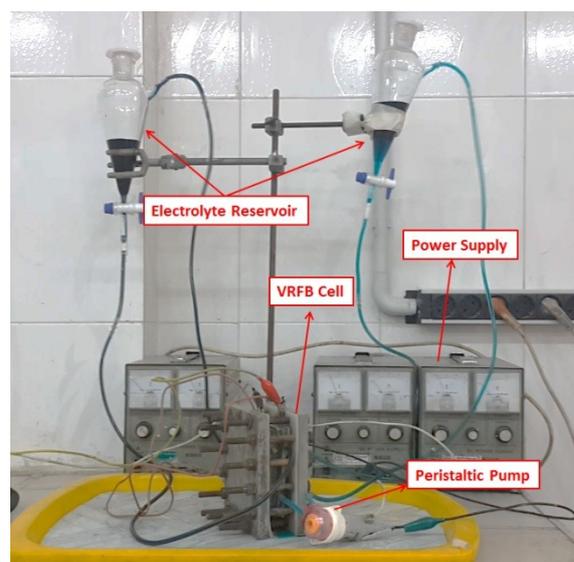


Figure 1. Laboratory unit of fabricated VRFB cell using an electrolyte of 1 M VOSO₄ in the optimized supporting electrolyte of 6 M HCl and 2.5 M H₂SO₄

3. RESULTS AND DISCUSSION

3.1. Wettability evaluation

Wettability studies usually involve the measurement of contact angles as the primary data, which indicates the degree of wetting when a solid and liquid interact. Small contact angles ($\ll 90^\circ$) correspond to high wettability, while large contact angles ($\gg 90^\circ$) correspond to low wettability. Fig. 2 shows the water contact angle images of PCF electrode. According to the

measurements, left and right angles are 115° and 112° , respectively; so the PCF electrode has low wettability and it can be considered as hydrophobic. The contact angle measuring of HCF electrode was impossible, because the HCF electrode absorbed water drop by its porous structure. Therefore, the hydroxylation process has changed the wettability property of carbon felt electrode and HCF has become a hydrophilic structure.

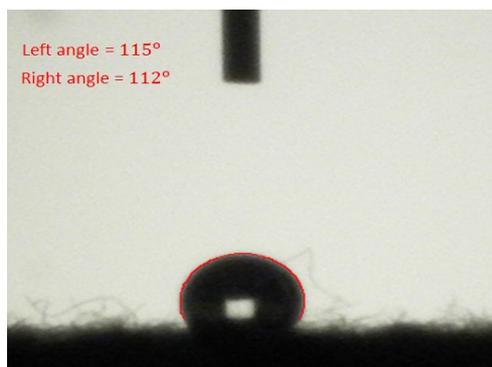


Figure 2. Result of contact angle measurement using water droplets on PCF electrode

The ability of the PCF and HCF electrodes to absorb the optimized VOSO_4 electrolyte was studied by measuring dry weight and wet weight of electrodes. Weight measurement data are reported in Table 1. The results indicate that the PCF electrode can absorb the optimized VOSO_4 electrolyte equal to its dry weight. The hydroxylation process has significantly improved absorption ability so that the HCF electrode absorbs the optimized VOSO_4 electrolyte more than four times of its dry weight. These results were in accordance with contact angle measurements.

3.2. The cyclic voltammetry studies

Cyclic voltammograms of PCF and HCF used as positive electrodes are shown in Fig. 3. The detailed parameters obtained from the CV curves are listed in Table 2. For the PCF electrode, the shapes of the

oxidation peak and the reduction peak are unsymmetrical, and the corresponding currents I_{pa} and I_{pc} are small, indicating that the electrochemical activity is relatively low. When the carbon felt is hydroxylated with a mixture of H_2SO_4 and HNO_3 , both oxidation and reduction peak currents are increased remarkably and the peak potential separation is decreased from 356 to 246 mV, suggesting that the electrochemical activity and the kinetic reversibility on HCF electrode are improved compared to the pristine one.

The oxidation peak current density has been increased for HCF electrode to 41 mA cm^{-2} (peak potential 0.974V) from 11 mA cm^{-2} for PCF electrode at the same potential. The current density indicates the rate of an electrochemical reaction; here, the number of VO^{2+} species turns into VO_2^+ at the electrode surface. Thus, in specific potential of 0.974 V, the rate of electrochemical reaction or the number of VO^{2+} species oxidized to VO_2^+ at the surface of HCF electrode is 3.7 times more than that of the PCF electrode.

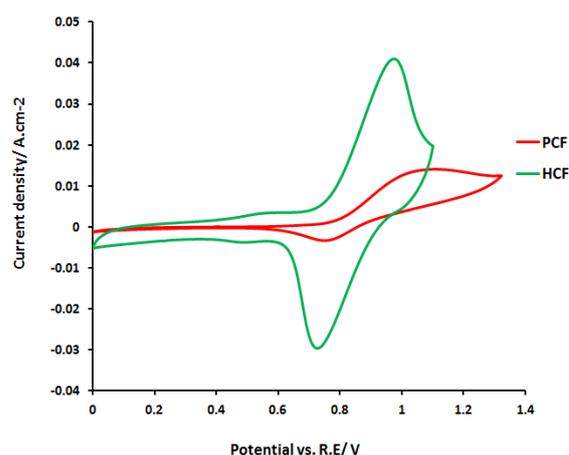


Figure 3. Cyclic voltammograms of PCF and HCF electrodes at scan rate of 5 mV s^{-1} in a solution of 0.2 M VOSO_4 with (0.5 M H_2SO_4 + 1.2 M HCl) supporting electrolyte

TABLE 1. Wettability parameters of modified electrodes in acidic solution of 0.2 M VOSO_4 + 0.5 M H_2SO_4 + 1.2 M HCl

Electrode	Dry weight (g)	Wet weight in optimized VOSO_4 electrolyte (g)	Absorption percentage of VOSO_4 (%)	Contact angle (deg)	
				Left	Right
PCF	0.2528	0.5216	106.3	115°	112°
HCF	0.4538	2.3017	407.2	Hydrophilic	

In order to ensure stability of the modified electrode, five consecutive potential scans were recorded for HCF electrode in the solution of 0.2 M VOSO_4 in (0.5 M H_2SO_4 + 1.2 M HCl). As it can be seen in Fig. 4, with regard to stability of the voltammograms, electrochemical reactions at the electrode surface have a good repeatability and the modified electrode does not show any destruction or instability in consecutive cycles. As Yue et al. [14] have investigated untreated

and hydroxylated carbon paper electrodes in non-optimized electrolyte for different hydroxylation times, the results of "5h hydroxylation" are compared with current work results. Their Cyclic voltammetry studies indicate that ΔE_p remains constant (at 350 mV) after hydroxylation of carbon paper electrodes for 5h. However, in the current study ΔE_p decreases about 30% (from 356 to 246 mV) which indicates faster electron transfer kinetics.

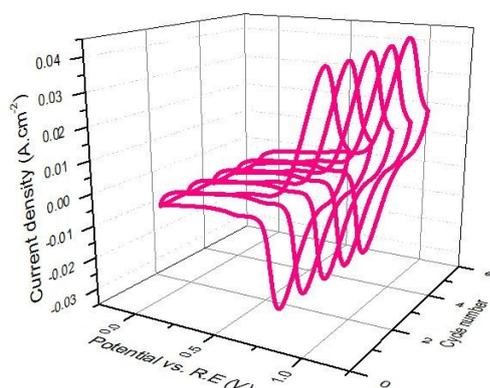


Figure 4. Five consecutive voltammograms at the HCF electrode in the solution of 0.2 M VOSO_4 with (0.5 M H_2SO_4 + 1.2 M HCl) supporting electrolyte at scan rate of 5 mV s^{-1}

Furthermore, in their investigation I_{pa} and I_{pc} increased to 2.37 and 4.1 times after hydroxylation of carbon paper electrodes for 5h (by using non-optimized supporting electrolyte). However, our results show that I_{pa} and I_{pc} increase about 3 and 9 times after hydroxylation of PCF electrode (by using optimized supporting electrolyte). These comparisons indicate that combination of both modification methods (i.e. using optimized supporting electrolyte and hydroxylation process of carbon felt electrodes) can be more effective to increase the system current in comparison with single hydroxylation method.

3.3. AC impedance spectroscopy studies

Fig. 5 displays the Nyquist plots obtained at open circuit potential of 0.7 V vs. Ag|AgCl in the solution of 0.2 M VOSO_4 and 0.2 M V_2O_5 with supporting electrolyte of (0.5 M H_2SO_4 + 1.2 M HCl). The high frequency semi-arc arose from the charge transfer reaction at the electrolyte/electrode interface. The radius of the semi-arc reflects the charge transfer resistance. It can be easily found that the semi-arc radius of HCF was much smaller than PCF electrode, which suggests a lower charge transfer resistance.

In order to investigate the electrode reaction process, the impedance spectroscopy was simulated by “NOVA” software and the equivalent circuit is shown in Fig. 5, where R_s is the solution resistance between reference electrode and work electrode, CPE is Constant Phase

Element about Faraday process, and R_{ct} is charge transfer resistance. Every equivalence element values are listed in Table 3. The results show that the charge transfer process was the controlling step of the electrode reaction. According to the equivalent circuit of PCF electrode, R_{ct} was calculated to be 648 Ω . The obtained charge transfer at HCF (176 Ω) shows a decrease of about 73 % in R_{ct} due to the hydroxylation on the PCF electrode surface.

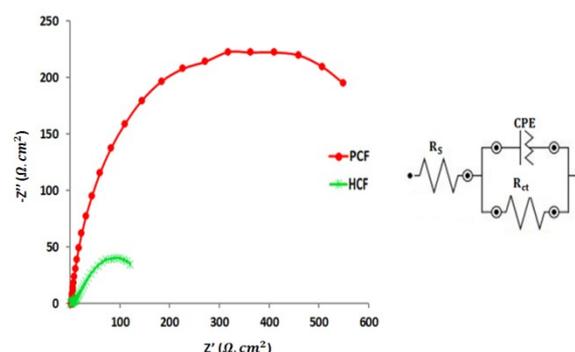


Figure 5. Nyquist plots of PCF and HCF electrodes in 0.2 M VOSO_4 + 0.2 M V_2O_5 in 0.5 M H_2SO_4 + 1.2 M HCl solution

In a potential close to the open circuit potential where the electrochemical conversion is in equilibrium, the exchange current (i_o) can be calculated by utilizing the following Equation (1) [15]:

$$i_o = \frac{RT}{R_{ct}nF} \quad (1)$$

where R is the universal gas constant, T is temperature in K, R_{ct} is charge transfer resistance, n is the number of exchanged electrons, and F is the Faraday constant. The lower the exchange current, the slower would be the redox reaction [16].

The values of the exchange current density (j_o) for PCF and HCF electrodes were calculated and reported in Table 3. The effect of hydroxylation is increasing of the exchange current, and the value of j_o for HCF is $1.59 \times 10^{-4} \text{ A cm}^{-2}$ that is nearly four times more than the quantity of j_o for PCF, which represents a significant increase in the reaction rate of VO^{2+} to VO_2^+ at the surface of HCF electrode.

TABLE 2. Parameters obtained from CV curves for the V(IV)/V(V) redox couple

Electrode	E_{pa} (V)	E_{pc} (V)	I_{pa} (mA)	I_{pc} (mA)	ΔE_p (mV)	I_{pa}/I_{pc}
PCF	1.106	0.750	14.05	3.35	356	4.19
HCF	0.974	0.728	41.01	29.67	246	1.38

TABLE 3. Parameters obtained from fitting the impedance plots of Fig. 5

electrode	R_s (Ω)	CPE		R_{ct} (Ω)	j_o (A cm^{-2})
		Y_o (mMho)	n		
PCF	3.25	0.79	0.82	648	3.96×10^{-5}
HCF	2.00	19.5	0.636	162	1.59×10^{-4}

3.4. FT-IR analysis

To inspect the surface chemistry of the carbon felt electrodes, we carried out FT-IR spectroscopy; the results are shown in Fig. 6. The functional group associated with -OH groups appears at 3450 cm^{-1} , and C=C-O groups have an absorption peak at 1615 cm^{-1} . The broader peak, which can be assigned to the C=O and the C-O groups, appears in the range of $1740\text{--}1800\text{ cm}^{-1}$. As can be seen in Fig. 6, the peak intensities significantly changed after hydroxylation and thermal treatment of PCF electrode and this is attributed to the increase in the number of the oxygen-containing functional group sites on the surface of the carbon felt.

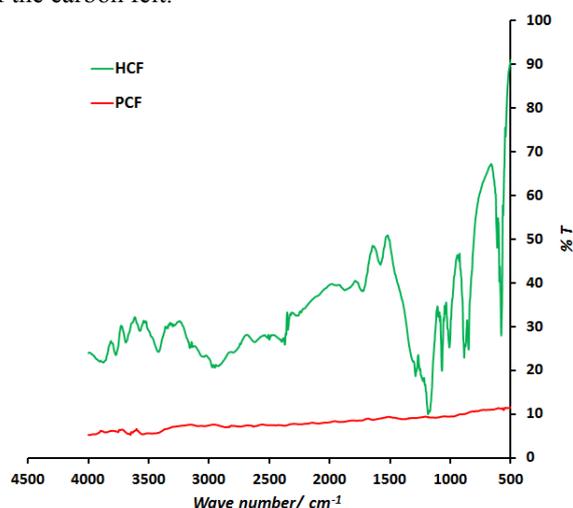


Figure 6. FT-IR spectra of PCF and HCF electrodes.

3.5. VRFB single cell performance

Fig. 7 presents the charge-discharge profiles of two cells assembled with the pristine carbon Felt (cell A), and carbon felt hydroxylated with mixture of H_2SO_4 and HNO_3 (cell B). The size of electrodes was $8 \times 8\text{ cm}^2$. Both cells were charged and discharged at a current density of 15 mA cm^{-2} . It can be seen that the profile of the cell A which uses HCF as electrode has a lower charge voltage plateau and a higher discharge voltage plateau, thereby achieving the higher voltage efficiency. The diffusion rates of charge species were significantly improved by using the HCF electrode inside the VRFB cell, so the Coulombic efficiency has been significantly increased. The detailed data obtained from charge-discharge profiles are summarized in Table 4 and Fig. 8. From this data it is evident that the difference between the maximum voltage of charge and OCV before discharge was significantly lower in cell A with HCF electrode. It means that the internal loss of the cell A was considerably lower than Cell B.

The energy efficiency of cell B was also more than four times with respect to cell A. The reason might be that the hydroxylation increases more oxygen-containing functional groups combined on the surface of the carbon felt electrode, and this treatment significantly reduced

activation loss of electrochemical reactions in the VRFBs [17]. The cell with higher internal loss consumed more additional energy during the discharge process. Therefore, the energy efficiency of cell A was much lower than cell B. Generally, the results of VRFB cell performance are consistent with cyclic voltammetry and impedance spectroscopy studies, and those confirm each other.

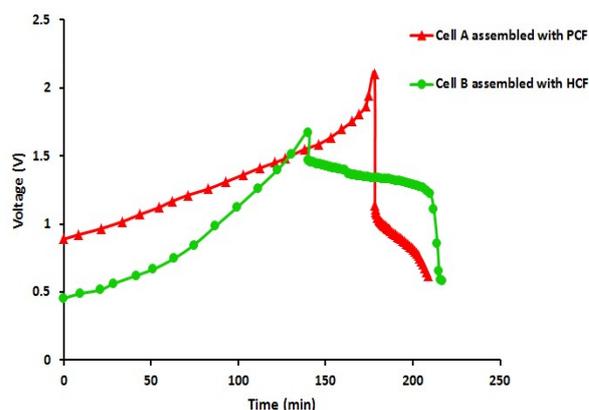


Figure 7. Charge-discharge profiles of two cells assembled with the PCF (cell A) and HCF electrodes (cell B).

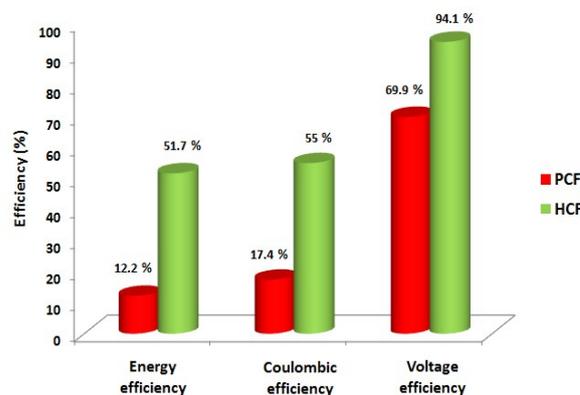


Figure 8. Comparison of cell efficiency values for cells A (assembled with PCF) and Cell B (assembled with HCF) at a charge-discharge current density of 15 mA cm^{-2} .

TABLE 4. Parameters obtained from charge-discharge profiles of Cell A and B.

Cell type	Cell A	Cell B
Charge time (min)	178	140
Discharge Time (min)	31	77
Maximum voltage of charge (V)	2.103	1.674
Open circuit Voltage before discharge (V)	1.471	1.575
Energy efficiency (%)	12.2	51.7
Coulombic efficiency (%)	17.4	55.0
Voltage efficiency (%)	69.9	94.1

4. CONCLUSIONS

In the present investigation, a mixture of six parts HCl and 2.5 parts H_2SO_4 was used as an optimized supporting electrolyte to prepare VOSO_4 solution for

vanadium redox flow battery. The PCF electrode was hydroxylated with mixed acids of H₂SO₄ and HNO₃ to be the cathode of VRFB in which optimized supporting electrolyte was used. The results indicated that the hydroxylation process has significantly improved the ability of PCF electrode to absorb the optimized VOSO₄ electrolyte. Furthermore, the oxidation peak current density has been increased for HCF electrode to 41 mA cm⁻² from 11 mA cm⁻² for PCF electrode at the same potential. Electrochemical impedance studies showed a decrease of about 73 % in charge transfer resistance due to the hydroxylation on PCF electrode surface. The results also indicated that energy, voltage and coulombic efficiencies were significantly improved by using the hydroxylated electrodes inside the cell of vanadium redox flow battery.

5. ACKNOWLEDGMENT

The authors thank Iranian Space Research Center for sponsoring this study.

REFERENCES

- Parasuraman, A., Lim, T.M., Menictas, C. and Skyllas-Kazacos, M., "Review of material research and development for vanadium redox flow battery applications", *Electrochimica Acta*, Vol. 101, (2013), 27-40.
- Rahman, F. and Skyllas-Kazacos, M., "Vanadium redox battery: Positive half-cell electrolyte studies", *Journal of Power Sources*, Vol. 189, No. 2, (2009), 1212-1219.
- Roe, S., Menictas, C. and Skyllas-Kazacos, M., "A high energy density vanadium redox flow battery with 3 M vanadium electrolyte", *Journal of The Electrochemical Society*, Vol. 163, No. 1, (2016), A5023-A5028.
- Liu, Q., Grim, G., Papandrew, A., Turhan, A., Zawodzinski, T. A. and Mench, M. M., "High performance vanadium redox flow batteries with optimized electrode configuration and membrane selection", *Journal of The Electrochemical Society*, Vol. 159, No. 8, (2012), A1246-A1252.
- Kabir, H., Gyan, I. O. and Cheng, I. F., "Electrochemical modification of a pyrolytic graphite sheet for improved negative electrode performance in the vanadium redox flow battery", *Journal of Power Sources*, Vol. 342, (2017), 31-37.
- Wang, W. and Wang, X., "Investigation of Ir-modified carbon felt as the positive electrode of an all-vanadium redox flow battery", *Electrochimica Acta*, Vol. 52, No. 24, (2007), 6755-6762.
- Liu, T., Li, X., Xu, C. and Zhang, H., "Activated carbon fiber paper based electrodes with high electrocatalytic activity for vanadium flow batteries with improved power density", *ACS Applied Materials & Interfaces*, Vol. 9, No. 5, (2017), 4626-4633.
- Sun, B. and Skyllas-Kazacos, M., "Modification of graphite electrode materials for vanadium redox flow battery application—I. Thermal treatment", *Electrochimica Acta*, Vol. 37, No. 7, (1992), 1253-1260.
- Sun, B. and Skyllas-Kazacos, M., "Chemical modification of graphite electrode materials for vanadium redox flow battery application—part II. Acid treatments", *Electrochimica Acta*, Vol. 37, No. 13, (1992), 2459-2465.
- Noack, J. and Tübke, J., "A comparison of materials and treatment of materials for vanadium redox flow battery", *ECS Transactions*, Vol. 25, No. 35, (2010), 235-245.
- Li, X.-g., Huang, K.-l., Liu, S.-Q., Ning, T. and Chen, L.-q., "Characteristics of graphite felt electrode electrochemically oxidized for vanadium redox battery application", *Transactions of Nonferrous Metals Society of China*, Vol. 17, No. 1, (2007), 195-199.
- González, Z., Sánchez, A., Blanco, C., Granda, M., Menéndez, R. and Santamaría, R., "Enhanced performance of a Bi-modified graphite felt as the positive electrode of a vanadium redox flow battery", *Electrochemistry Communications*, Vol. 13, No. 12, (2011), 1379-1382.
- Li, L., Kim, S., Wang, W., Vijayakumar, M., Nie, Z., Chen, B., Zhang, J., Xia, G., Hu, J. and Graff, G., "A Stable Vanadium Redox-Flow Battery with High Energy Density for Large-Scale Energy Storage", *Advanced Energy Materials*, Vol. 1, No. 3, (2011), 394-400.
- Yue, L., Li, W., Sun, F., Zhao, L. and Xing, L., "Highly hydroxylated carbon fibres as electrode materials of all-vanadium redox flow battery", *Carbon*, Vol. 48, No. 11, (2010), 3079-3090.
- Bard, A.J. and Faulkner, L.R., "Fundamentals and applications", *Electrochemical Methods*, 2nd ed.; Wiley: New York, (2001).
- Lefrou, C., Fabry, P. and Poignet, J.-C., "Electrochemistry: the basics, with examples", Springer Science & Business Media, (2012).
- Conway, B. and Jerkiewicz, G., "Nature of electroadsorbed H and its relation to metal dependence of catalysis in cathodic H₂ evolution", *Solid State Ionics*, Vol. 150, No. 1, (2002), 93-103.