Optimization of thermal oxidation of electrodes for the performance enhancement in all-vanadium redox flow batteries

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A comprehensive study of the thermal oxidation of PAN-based carbon felts and its optimization for the negative half-cell of the all-vanadium redox flow battery

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Abstract

Thermal oxidation of a graphite felt in air is the most widely used electrode activation method to enhance the performance of a vanadium redox flow battery. It has been reported extensively, but almost all previous studies used individual treatment protocols with only few parameter variations. In this paper, treatment time and temperature were varied systematically along with in-depth physicochemical and electrochemical analysis. Prolonged treatment time is chosen for oxidation at lower temperatures aiming at low material loss rates, whereas shorter periods are applied at higher treatment temperatures, which are associated with elevated material loss. Among the

electrodes treated with various protocols, the best performance is observed with electrodes oxidized at 750°C for 5 minutes. This study is important for both, reproducibly preparing samples at lab scale as well as commercial developers, where optimized and cost-effective pretreatment plays a significant role.

1. Introduction

Renewable energy sources have attracted much attention in the last decade, owing to their low environmental impact. Unfortunately, the electricity generation from renewable energy sources is inherently intermittent [1]. These issues can be resolved only with appropriate energy storage systems. The vanadium redox flow battery (VRFB) is one of the promising technologies for large scale units, due to its stable performance, long life, safety and design flexibility [2-4]. The active mass is based on four different states of vanadium, thus avoiding the risk of cross-contamination of the active species [3, 5]. Unfortunately, the VRFB suffers from low specific energy, prompting numerous efforts towards improving its energy efficiency and specific energy. Key areas in VRFB research include the development of components such as, electrodes [6-14], membranes [15-17] or electrolytes [18-20], as well as studies with respect to cell design and modelling [21-23] and performance monitoring of cell and stacks [18, 24-28].

The energy efficiency of the battery largely depends on the electrocatalytic properties of the carbon electrodes, as the redox reactions of the vanadium ions occur at the surfaces of the two electrodes. Graphite felts have become the electrode material of choice owing to their high surface area, good stability and good electronic conductivity. Pristine graphite felts, however, are inherently hydrophobic and, hence, display poor charge-transfer kinetics due to insufficient utilization of the porous electrode [2, 29, 30]. As a result, various modification methods have been adopted to

activate graphite felts including thermal [30-33], wet chemical [34, 35], corona discharge [36], microwave [37], gamma-ray irradiation [30]. Among these, thermal treatment of the graphite felt is most common in commercial applications.

Sun et al. pioneered the thermal treatment of the graphite felts for VRFB [31]. They carried out oxidation in air at different temperatures for 30 h and observed the highest cell efficiency using electrodes treated at 400°C. This gain in cell performance was attributed to the presence of surface oxygen groups on the fibres. Similar findings have been reported by Kim et al. for the oxidation of the carbon felt at 500°C for 5 h [30]. Thermal treatment strategies were further investigated using different mixed gas compositions, which led to changes in electrode properties [38]. A profound mechanistic understanding of the role of different parameters, however, is still lacking. Most of the antecedent studies invoke the following aspects (i) increase in number of functional groups on the surface of the carbon fibre [31, 32, 39], (ii) increased amount of edge sites [32, 40], (iii) increase in wettability [40] and an enhanced surface area.

Furthermore, recent studies have disproven the universal benefits of felt oxidation and revealed, that it even produces contrary effects on the electrochemistry of the positive ($\text{VO}^{2+}/\text{VO}_2^+$) and the negative ($\text{V}^{2+}/\text{V}^{3+}$) redox couples. Friedl et al. investigated the positive redox couple reaction on multiwall carbon nanotubes decorated with different amount of surface functional groups and their results showed that the positive redox couple rate constant decreases with the amount of the surface functional groups [41]. Schweiss et al. similarly reported that excessive surface oxidation of PAN and rayon-based carbon felt induced a slightly detrimental effect on the positive redox couple while improving the kinetics of the negative half-cell [42]. Langner et al. determined the overpotentials by placing reference electrodes at the inlet and outlet of the cell, and observed no change in overpotential in the positive side by using pristine or thermally oxidized carbon felts

[43]. They concluded that the charge transfer in the positive half-cell is governed by electronic conductivity of electrodes and the effects of surface functional groups are negligible.

By contrast, there is a consensus that oxidative pre-treatment of the negative electrode enhances its electrochemical activity. Langner et al. [32] graphitized the samples at different temperature and later oxidized the samples from 400°C to 600°C in air. They reported that the amount of oxygen containing functional groups correlates with the defects of carbon fibres and decreases with increase in graphitization temperature. For identical thermal oxidation temperature fibres graphitized at low temperatures exhibited higher reactivity. The induced structural defects (i.e. higher sp^3 content and oxygen containing functional groups on the surface) facilitate the adsorption of the active species, which, in turn, accelerates the charge-transfer kinetics. Similarly, Greco et al. varied the treatment temperature from 400°C to 500°C by holding the time constant for 30 h, and found the optimum performance at 475°C [44].

Previous studies, however, fall short of a comprehensive analysis of the effects of treatment temperature and duration. In this study, we performed a systematic investigation of effect on thermal oxidation of PAN-based graphite felts on its performance at the negative electrode of the VRFB. Given the complexity of surface reactions on carbon and in order to rule out effects of impurities and variable felt properties, we studied PAN-based graphite felt from a single production batch. The temperature and duration of the oxidation step were selected from three distinct temperature regions in the thermogravimetric curve. The results from ex-situ characterization techniques (XPS, XRD, Raman, SEM, BET) are employed to identify the relevance of different material properties, such as surface composition, specific surface area, defects, mass loss or surface morphology.

Finally, based on the results of both ex-situ and in-situ investigations, an optimal electrode treatment temperature and time is recommended.

2. Experimental

2.1 Thermal oxidation of electrodes

Commercial battery grade carbon felt (Type SIGRACELL GFD 4.6 EA, SGL Carbon GmbH, Meitingen, Germany) produced from a single batch was used for this study. The samples were washed with ethanol and deionized water, and dried under vacuum. The precleaned electrodes were thermally oxidized under air in a muffle furnace (Nabertherm GmbH, Lilienthal, Germany). The samples were heated at a rate of $5^{\circ}\text{C min}^{-1}$ until the desired temperature was reached. After holding at the given temperature for the given period, the samples were removed after cooling to ambient temperature. For electrodes treated at 750°C , the furnace was pre-heated to 750°C and the electrode was inserted into the furnace for a defined period. Afterwards, the electrode was directly removed to the ambient. For each experiment, the pre-treatment of the electrode was performed right before conducting any subsequent analysis.

2.2 Material characterization

X-ray diffraction (XRD) patterns were obtained by using a Shimadzu (XRD-6000 setup) X-ray diffractometer with Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$) operated at 40 kV and 30 mA. The morphology of the electrodes was characterized by field emission-scanning electron microscopy, FE-SEM (JEOL, Model JSM-7600F) with an acceleration voltage of 5 kV. Raman spectra were recorded by a Confocal Raman spectrometer at 488 nm (Witec alpha 300 SR). X-ray photoelectron spectroscopy (XPS) was performed, using a Model- AXIS SupraTM with monochromatic Al K α

(energy 1486.71 eV) operated at 15 kV and 5 mA. The peak area was determined by fitting to Gaussian-Lorentzian functions. BET surface area was determined by Krypton adsorption using an Autosorb™ setup (Quantachrome, Odelzhausen, Germany).

2.3 Electrochemical characterization

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed employing a three-electrode configuration using a VMP3 electrochemical workstation (BioLogic, Netherlands). An electrode with a geometric area of 1 cm² and a graphite current collector (SIGRACELL® PV10, SGL Technic LLC, Valencia, CA, USA) were compressed in a purpose-built PVC holder and served as the working electrode. A saturated mercury sulfate electrode (SMSE, Hg|Hg₂SO₄|sat. K₂SO₄, E₀ = 0.64 V) and platinum mesh were used as the reference and counter electrodes, respectively. CV was performed within a potential range from -0.7 V to -1.25 V vs SMSE at a scan rate of 5 mV s⁻¹. Prior to the electrochemical measurement, electrodes were immersed in the electrolyte to be fully imbibed with electrolyte. The thermally oxidized electrodes were immediately wetted as soon as they were in contact with the electrolyte. For the sake of uniformity, all felts were handled with the same procedure. Electrochemical impedance spectra were recorded in a frequency range from 10⁵ Hz to 10⁻² Hz with an AC amplitude of 10 mV. Both CV and EIS were performed with the electrolyte containing 1.6 M V²⁺/V³⁺ in 4 M sulfate at 50% state of charge (SOC) at open circuit potential. Using the same three-electrode configuration, double layer capacitance (DLC) was determined. CV was performed in the 4 M H₂SO₄ at the scan rate of 10, 20, 50 and 100 mV s⁻¹. The current within the non-faradaic region at around 0.2V was used for the calculation. The capacitance was obtained from the slope of the double layer charging current vs scan rate. Nitrogen gas was purged throughout the experiment to create an inert atmosphere. The temperature of the electrolyte was kept 25°C throughout the experiments.

2.4 Flow cell testing

An in-house fabricated flow cell with an area of 20 cm² (5 cm x 4 cm) was used for investigation of the VRFB cell performance. As-received graphite felt was employed as the positive electrode, whereas the materials of the study were placed at the negative side. Cells were assembled using graphite current collectors (PV10, SGL Technic Inc., Valencia, CA, USA), anion exchange membranes (Fumasep FAP 450®, Bietigheim, Germany), copper current collectors and silicon gaskets. To maintain consistency in terms of the electrode compression (25% with respect to the virgin thickness) throughout all experiments, a torque wrench was used during the cell assembly. Each electrolyte tank was filled with 100 mL of VRFB electrolyte containing 1.6 M V^{+3.5} in 4 M sulfate purchased from GfE (Nuremberg, Germany). Two peristaltic pumps continuously supplied VRFB electrolyte at a flow rate of 60 mL min⁻¹. A constant electrolyte temperature was maintained at 24±1 °C throughout the measurements. A paraffin oil layer was placed on the surface of the electrolyte to prevent the aerial oxidation of V²⁺. The cell was charged and discharged at current densities ranging from 60 to 100 mA cm⁻² using a battery charger (NEWARE, China, 10 V/10 A). The long-term performance was monitored by running 60 charge-discharge cycles at a current density of 80 mA cm⁻². Cell cycling was conducted between cell voltage margins of 0.9 V (lower cut-off) and 1.65 V (upper cut-off).

3. Results and discussion

3.1 Thermogravimetric analysis

The temperature ranges were selected based on the result of TGA analyses (Figure 1a). The first zone at around 400°C is characterized by minor mass losses due to desorption of adsorbed

impurities and moisture. For the samples treated at 400°C, the oxidation time was varied from 10 to 30h. For temperatures ranging from 500°C to 600°C, we kept the treatment period constant at 5 h. Finally, to observe the changes occurring at a higher temperature, a temperature of 750°C, which is within the zone of rapid decomposition, was selected. To avoid massive degradation, excessive felt etching, fibre breakage and decrease in mechanical and electrical conductivity, the treatment time of the electrode at this temperature (750°C) was fixed at 5, 10 and 15 mins, respectively. The mass loss due to oxidation was calculated by weighing the electrodes before and after thermal treatment. The prefix T denotes the oxidation temperature, suffix h and m denote the hours and minutes, respectively. GF represents the pristine graphite felt from the manufacturer.

Figure 1. (a) Thermogravimetric analysis in air (heating rate of 10°C min⁻¹) of a pristine graphite felt (b) mass loss of the electrode/graphite felt as a function of oxidation temperature and time.

Figure 1-b shows the weight loss of graphite felt samples exposed to different oxidation temperatures and different periods. The mass loss is insignificant for the felt treated at 400°C, but increases with temperature (even if exposed for shorter intervals). CO₂ evolution occurs with progressive mass loss. The active sites on the surface of the carbon fibre form oxygen-containing functional groups, eventually releasing CO₂. The stepwise mechanism, as shown in Figure 2 for

the graphite fibre surface oxidation has been widely investigated [45, 46]. The edge planes of the graphite lattice act as electron donors which could support the dissociation of molecular oxygen into oxygen atoms which react with the carbon ultimately leading to partial gasification.

Figure 2. Stepwise progressive oxidation mechanism for graphite fibre surface.

3.2 Analysis by SEM, XRD and Raman

All materials were analyzed by XRD and SEM as shown in Figure 3. The characteristic diffraction peak is at 25.6° , corresponding to the (002) plane. In addition, two smaller peaks can be observed at 43.1° and 53.5° , corresponding to the (100) and (004) planes, respectively. An increase in oxidation temperature leads to a slight decrease in diffraction intensity. The peaks are distinct for as-received graphite felt (GF), but a minor drop in intensity is observed with increasing temperature and duration of treatment. The fading intensity of diffraction might point at defects generated on the surface. This is rather surprising, as the carbon fibres have been graphitized above a temperature of 2000°C , and thus a change in bulk properties due to thermal oxidation is unlikely. The interlayer spacing (d_{002}) and crystallite stacking height (L_c) were calculated using the Scherrer equation (plots of d_{002} and L_c are provided in Figure S1). It is observed that d_{002} ($3.46 \text{ \AA}$ of the pristine fibre, GF) increases with increasing oxidation temperature and reaches a maximum of $3.52 \text{ \AA}$ for sample T600-5h while L_c remains almost constant. Oxidation of the edge planes of the crystalline domains obviously induces a minor expansion of the lattice without changing its stacking height.

Figure 3. (a) X-ray diffractograms pattern of the graphite felt treated at various oxidation temperature (b) FESEM image of carbon fibres oxidized at various oxidation temperature.

For further investigation, SEM images of carbon fibre were taken (Figure 3-b). Whilst the fibre surface of the virgin material (GF) is very smooth, visible morphological changes emerge after

thermal oxidation (increase in surface roughness). For T600-5h and T750-15m, even small cavities and incipient delamination were observed.

The electrolyte uptake of the electrodes was evaluated by simple wetting tests as shown in Figure 4-a. Electrolyte droplets at different sizes are formed resulting from the higher contact angle for the electrodes which are not activated or partially activated. The droplets on the surface of the GF and the T400 series samples retain their shape. Absorption was gradual for the sample T500-5h, as traces of the electrolyte remain on the surface. By contrast, immediate electrolyte uptake was observed for the other samples. Admittedly, this straightforward tests provide only qualitative information about the characteristics of electrode/carbon fibre before and after oxidation.

The graphitic character of the fibre surfaces was determined with confocal Raman spectroscopy. The first order Raman mode, also known as G band (graphitic) appeared at around 1585 cm^{-1} corresponding to sp^2 carbon. Similarly, the D band (disordered) which reflects the amorphous carbon domains originating from a second order scattering appeared at around 1355 cm^{-1} [47]. Raman spectra of the GF reveals the two distinct peaks of G and D band as shown in Figure 4-b. However, the activated electrodes showed reduced G band and increased D band intensities with a broadening of two peaks as shown in Figure 4-c. The enlarged spectrum allows for fitting additional peaks at 1210 cm^{-1} (D'') and 1510 cm^{-1} (D'), which could be assigned to disordered graphitic domains or amorphous carbon, respectively [48]. The change in the structural ordering and crystallinity is analysed by the intensity ratio between the $\text{I}_\text{D}/\text{I}_\text{G}$ bands. The penetration depth of the 488 nm laser is about 50 nm [49], as the exact confocal penetration depends on the instrumental and sample parameters. Hence, the Raman spectra reflect the crystallinity of the fibre surface only. Figure 4-d presents the ratio of intensity for D to G band for all of the samples, ascribing the increase in this value to an increase in surface defects or decrease in graphitic

domains. Therefore, the ratio increased with increase in temperature and exposure time. The highest defect density is observed for the samples treated at T550-5h, T600-5h and T750 series.

Figure 4. (a) Optical images of electrolyte droplets at various carbon felts (b) Raman spectra for the as received electrode (c) Raman spectra for electrode pre-treated at T550-5h (d) ratio of an intensity of D band to G band.

The intensity ratio I_D/I_G also allows for the calculation of the crystallite size (L_a) according to literature [50]. Values are plotted along with d_{002} and L_c from XRD in Figure S1. With the progressive material loss, a decrease of L_a was observed. The low values for T750-15m and T600-

5h directly correlated with the degree of burn-off. This behaviour might reflect the removal of C atoms from the edge of the crystallites.

3.3 Electrochemistry (single electrodes)

The negative half-cell reaction was investigated by cyclic voltammetry (CV) for the various electrodes (Figure 5). The negative vertex peak potentials of the CV were selected in order to avoid the hydrogen evolution reaction (HER) which might hamper the observation of the V^{2+}/V^{3+} reaction by forming bubbles on the surface of the electrode as well as blocking the diffusion of reactant to the surface.

Figure 5. CV scans recorded at 5 mV s^{-1} for as-received and thermally oxidized electrodes in negative redox couple electrolyte.

As can be observed from Table 1, an increase in oxidation temperature (T550-5h to T750-5m) reduces the peak separation (minimum for the T550-5h sample). The lowest values are found for T550-5h, T600-5h and T750-5m samples indicating high rates of charge transfer.

Table 1. Peak separation in CVs for various electrodes.

Sample	ΔE_p (V)
GF	0.52
T400-10h	0.5
T400-20h	0.51
T400-30h	0.49
T500-5h	0.37
T550-5h	0.24
T600-5h	0.27
T750-5m	0.26
T750-10m	0.30
T750-15m	0.30

In the classical electrochemical treatise, the reaction occurs at the surface of a planar, 2-dimensional electrode. For porous electrodes, classical interpretation of voltammetry and impedance spectroscopy cannot be applied. For instance, the electrochemical reaction rate might exceed the diffusion rate within the pore and thus become the rate-limiting step. The transmission line model describes the stepwise flux of ions within a pore [51]. The equivalent circuit in the system is simulated using an anomalous diffusion element or Bisquert diffusion element as shown in Figure S2. It is evident from the impedance spectra (Figure 6) that the reaction is under mixed control (diffusion and charge transfer). Fitting results are shown in table 2. The Ohmic resistance of the porous electrode is obtained from the high-frequency intersection point of with the x-axis

(R_b), the diameter of the semicircle provides the charge transfer resistance (R_{ct}), and the inclined line at low frequencies represents the ion diffusion in a pore of the electrodes.

Figure 6. Impedance spectra (Nyquist diagrams) obtained for pristine and thermally treated electrodes.

As expected, the largest R_{ct} was found for GF, whereas the values substantially decrease for the treated materials. It can be concluded from the R_b values that oxidation hardly influences the electronic conductivity of the electrodes. The constant phase element (Q) increases with the oxidation temperature, indicating an enhanced double layer capacitance due to the higher surface area.

Table 2. Results from fitting of the impedance spectra of different felt electrodes

Sample	$R_b (\Omega)$	$R_{ct} (\Omega)$	$Q (F.s^{(a-1)})$	a
GF	1.54	12.29	1.25E-03	0.91
T400-10h	1.52	5.86	1.41E-03	0.88
T400-20h	1.49	1.66	8.43E-03	0.86
T400-30h	1.51	1.51	1.80E-03	0.77
T500-5h	1.52	0.32	9.00E-02	0.65
T550-5h	1.50	0.13	1.12E-02	0.51
T600-5h	1.50	0.15	8.20E-02	0.53
T750-5m	1.50	0.15	1.40E-02	0.63
T750-10m	1.50	0.29	7.81E-02	0.61
T750-15m	1.50	0.27	3.80E-02	0.72

Double layer capacitance (DLC) is a quantity which not only reflects the total surface area but also depends on the electronic structure of the carbon surface [52]. The double layer capacitance for edge and basal plane on highly oriented pyrolytic graphite (HOPG) differs between 50-100 $\mu F cm^{-2}$ and 1-3 $\mu F cm^{-2}$, respectively [53-55]. The high value for the edge plane is possibly due to microfissures or partial ion intercalation [52, 55]. The low DLC of graphite basal plane in contact with electrolyte is most likely caused by a space charge capacity (C_{sc}) being smaller than the Helmholtz layer capacity (C_h) [56]. Overall, a distinct correlation exists between DLC and the number of exposed edge planes and lattice defects [52]. The DLC values for different samples are shown in Table 3.

Table 3. Gravimetric double layer capacitance, BET surface area and the specific double layer capacitance (normalized by the BET surface area) for the GF and thermally oxidized samples.

Sample	DLC ($\mu\text{F mg}^{-1}$)	BET ($\text{m}^2 \text{g}^{-1}$)	DLC/BET ($\mu\text{F cm}^{-2}$)
GF	20.0	0.37	5.4
T400-10h	68.3	0.7	9.76
T400-20h	145.0	1.53	9.47
T400-30h	213.3	3.01	7.08
T500-5h	575.5	15.1	3.07
T550-5h	1090.1	9.22	11.80
T600-5h	909.0	6.46	14.07
T750-5m	819.7	4.61	17.70
T750-10m	642.0	6.07	10.57
T750-15m	309.7	2.82	10.98

The largest DLC was determined for sample T550-5h. BET values from Table 3 show that the oxidation of electrodes leads to a large increase in surface area and follows almost the same behaviour as that of the DLC. The largest BET value was found for the T500 sample with an area of $15.1 \text{ m}^2 \text{g}^{-1}$ as compared to GF with an area of $0.37 \text{ m}^2 \text{g}^{-1}$. Since the DLC value is directly proportional to the surface area, normalization was done using the BET surface area (Table 3).

3.4 XPS analysis

The elemental composition and the nature of the functional groups on the electrode surface were evaluated by means of X-ray photoelectron spectroscopy (XPS). The spectra showed the presence

of carbon and oxygen only, as shown in Figure S3. The O1s peak intensity is low for the GF, but becomes more pronounced with the thermal modification. The atomic % values of both carbon and oxygen are presented in Table 4.

Table 4. Surface composition obtained from XPS in atomic %, the percentage of sp² C-content obtained from C1s peak, and functional groups obtained from the deconvolution of the O1s peak.

Sample	Oxygen (%)	Carbon (%)	O/C	C=C	C-O	C=O
GF	1.31	98.69	0.013	56.11	75.7	24.2
T400-10h	2.79	97.21	0.029	55.59	37.5	62.4
T400-20h	3.23	96.77	0.033	52.22	37.8	62.1
T400-30h	3.55	96.45	0.037	50.26	45.6	54.3
T500-5h	3.86	96.14	0.040	48.15	25.3	74.6
T550-5h	5.40	94.60	0.057	49.40	19.2	80.8
T600-5h	6.60	93.40	0.071	45.81	16.4	83.6
T750-5m	6.00	94.00	0.064	50.10	62.6	37.4
T750-10m	4.16	95.84	0.043	49.56	78.3	21.7
T750-15m	5.01	94.99	0.053	47.25	82.0	17.2

Overall, an increasing temperature produces an increased O/C atomic ratio. For sake of quantification, the C1s spectra were deconvoluted to obtain the various components, graphitic carbon C=C (284.5 eV), hydrocarbons C-C (285 eV), C-O (286.5 eV), C=O (288.3 eV) and π - π^* (291 eV) peak of graphite (Figure S4) [57]. The clear trend of increase or decrease of either C-O or C=O could not be observed from C1s spectra.

Figure 7. Deconvolution of O1s spectra of different samples.

C-O (532.5 eV) and C=O (531.5 eV) groups were quantified by deconvolution of the O1s band fine structure [58]. It is verified that prolonged oxidation results in a higher amount of carbonyl (-C=O) functional groups. By contrast, GF and the electrodes of the T750 series exhibited a higher content of the C-O functional group (Table 4). It is well established that the C-O groups are formed by the breakage of C=C bonds and that prolonged oxidation favours the formation of carbonyl functional group. Hence, it is very hard to explain that either of the two or only one functional groups is responsible for the performance gain. Nevertheless, the overall increase in oxygen containing functional groups has been reported to catalyze the negative half redox reaction [34, 59].

3.5 Single cell VRFB tests

For the evaluation of flow cell performance, charge-discharge cycling tests were carried out using the different materials as the negative electrode (current densities from 60 mA cm⁻² to 100 mA cm⁻²). Energy efficiency (EE) and voltage efficiency (VE) of a VRFB single cell containing different felt at the negative electrodes are shown in Figure 8. It can be seen that the lowest values for EE and VE are observed for the GF sample. The low wettability (oxygen content) is responsible for the poor performance. Increasing oxidation time significantly increased the EE and VE for the T400-20h and T400-30h samples. At a current density of 100 mA cm⁻², a significant increase (~12%) of EE and VE is observed as compared to the GF samples. The EE and VE of T500-5h, T750-15m and T750-10m samples are within a 1.5% range, indicating almost the same level of cell performance. Superior performance is shown by the T550-5h, T750-5m and T600-5h samples, respectively. At 100 mA cm⁻², the significant increase of (~17%) in EE as compared to the value for the GF sample is observed.

Figure 8. Performance of VRFB cell at various current densities, showing (a) energy efficiency (b) voltage efficiency (c) area specific resistance.

The area specific resistance (R_a), which represents the average cell resistance during the charge-discharge cycling, is a suitable figure of merit to compare the performance of VRFB cells. The average, area-specific cell resistance (R_a) during the cell charging/discharging is calculated using

$$R_a = \frac{V_{oc}}{j_{app}} \cdot \left(\frac{1-VE}{1+VE} \right) \quad (1)$$

where j_{app} , VE , and V_{oc} represent the applied current density, the voltage efficiency and the average open circuit voltage (~ 1.38 V at 25°C) during charging and discharging, respectively. As the

membrane resistance and contact resistance were assumed to be invariant, a change in R_a reflects the change in charge transfer resistance. The trend with respect to R_a is in excellent agreement with the charge transfer resistance (R_{CT}) obtained from the EIS of electrodes (Figure 6). Consequently, the benefits with respect to battery performance are solely due to the use of sufficiently activated graphite felt electrodes in the negative half-cell. Next, 60 consecutive charge-discharge cycles at a constant current density of 80 mA cm^{-2} were run to evaluate the effects of the treatment on the durability. The coulombic efficiency (CE), VE and EE are shown in Figure 9. A comparison of the voltage profile vs specific capacity (Ah L^{-1}) also showed the similar result (Figure S5). The significant shift in discharge curve is observed for the T550-5h, T750-5m and T600-5h samples. Under fixed cut off voltage between 0.9 V to 1.65 V, the use of GF and T400-10h samples resulted in relatively poor specific capacity ($\sim 4.5 \text{ Ah L}^{-1}$). With the thermal treatment, for T550-5h, T750-5m and T600-5h samples, the specific capacity increase to $\sim 7.5 \text{ Ah L}^{-1}$.

Figure 9. Cycling performance of VRB cell at 80 mA cm^{-2} for 60 cycles (a) Coulombic efficiency (b) energy efficiency (c) voltage efficiency.

Long term cycling tests (Figure 9) confirmed the trends observed in the foregoing screening tests (Figure 8). There is no notable reduction in energy efficiency during extended cycling, suggesting that the beneficial effect of thermal treatment is preserved. The minor decrease in efficiency with progressive cycling is due to the active species crossover through the membrane and can be easily recovered by the rebalancing of the electrolyte. As shown in Figure 10, the cell cycling results are consistent with the results obtained from the single electrode measurement and allow for an unambiguous correlation with the physical characterization.

Figure 10. Correlation between the VE (at 80 mA cm⁻²), oxygen content, DLC and charge transfer resistance (R_{CT}).

4. Conclusions

A systematic analysis of the effects of thermal oxidation of graphite felts in air on their surface and structural properties have been carried out and placed into context with their resulting performance as negative electrodes in vanadium redox flow batteries. Benefits with respect to electrochemical characteristics could not be attributed to the presence of singular surface oxygen complexes. On the contrary, a clear correlation between the double layer capacitance, which is a

measure of the density of highly reactive edge planes or defects, and the cell performance could be verified.

The most practical value of this study is the understanding that short treatment intervals at harsh oxidation conditions constitute a viable option to reproducibly produce well-performing materials in a very cost-effective fashion.

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