



Variability within a single type of polyacrylonitrile-based graphite felt after thermal treatment. Part I: physical properties



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ABSTRACT

Graphite felts are often activated thermally before use in electrochemical reactors. This has the effect of improving wetting and decreasing charge-transfer resistance. In this work examination is made of the range of properties that arise within two different production charges of the same material from a single supplier. Although, it is clearly critical to know the variance within a single activated felt in order to make a fair comparison among different types of felt, this has been overlooked in previous such studies. Considerable variations were observed between two polyacrylonitrile (PAN) based felts from different production charges after thermal activation, despite both charges being of the same type of felt from one supplier. Particularly, one charge of felt lost considerably more mass and increased more in electrical double layer capacitance, on activation at a given temperature, than the other. To understand the cause of these differences the felts were examined as supplied and then after heat treatment over a range of temperatures. In the first part of this study the physical and morphological aspects of the felt are explored, before and after activating at temperatures of up to 575 °C in air.

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1. Introduction

A high overvoltage for hydrogen and oxygen evolution at graphite offers a broad electrochemical window in aqueous electrolytes. Carbon and graphite felts are moderate electrical conductors, highly porous, have high chemical stability under many conditions, and have relatively large surface areas. This combination of attributes makes them convenient for use as electrodes in electrochemical flow reactors. Unfortunately pure graphite has a low wettability and pre-treatment is necessary for most applications. Especially for redox flow batteries a good wettability is required to ease release of gas bubbles from the electrodes and ensure flow uniformity, as well as to ensure low flow resistance through the cells.

In the literature there are many reports of pre-treatments for felt electrodes by, for example, plasma [1,2], ultrasound [3] or thermal treatment [4–6], as well as electrochemical [7–9], wet chemical [10–12], hydrothermal [13], gamma ray [14] or gas phase

modification [15]. Of these methods thermal activation in air lends itself readily to commercial application and is the method of choice in this work. It is also one of the most widely reported activation techniques for graphitic felts for flow battery applications.

Published studies are often focused on obtaining optimal results for use in a redox flow cell, e.g. to give the lowest cell resistance. Many pioneering reports by the group of M. Skyllas-Kazacos have given a detailed investigation of chemical and structural composition of different felts and activation methods. Sun et al. point out the importance of C–O and C=O functional groups as active sites, which can be established by thermal and chemical activation [4,12]. Zhong et al. give a comparison between rayon- and PAN-based graphite felts, whereas the later one is better suitable for VRFB-applications which is referred to a higher content of C–O groups [16]. In contrast Mohammadi et al. show that electrical overcharge leads to a further increase of surface groups and increases the cell resistance [17]. Although many of these studies identify detailed differences between either the type of graphite felt used or the method of activation, in general these studies are limited to single batches of felts and the variability range of any one material itself has not been taken into account. All in all no conclusive picture can be drawn from the studies which type of felt or activation generally is the best. Where multiple measurements of a felt have been made, it may be assumed that

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these were performed on felts of a single production charge, which tend to behave very similarly during thermal activation. In contrast to many previous studies on graphite felts our focus lies in the reproducibility of the activation within a single felt type. However, there is a NASA report that mentions the difficulty arising from variations between felt lots, that were ostensibly the same, with respect to forming catalysed electrodes for the Cr(II)/(III) redox reaction [18]. The aim of our work is to understand and to minimize the variances of the pre-treatment.

It should be explained that graphite felt is produced in a number of stages, including: synthesis of the polyacrylonitrile (PAN), forming fibres and then non-woven material, needling to produce a felt, carbonising and finally high temperature pyrolysis. A large area of material is typically graphitised in a single production run, which we will refer to as a charge. In theory any of these manufacturing steps could lead to subtle differences in the final product, especially considering that felt producers specify only a range of bulk physical properties, such as area density, thermal conductivity, thickness and porosity.

Earlier studies with rayon-based felts were carried out at temperatures between 200 °C and 500 °C with heating durations between 10 to 50 hours in air [3,19]. In this work an optimum was found after heating at 400 °C for 30 h. Additionally the rate of mass loss during activation appeared to accelerate with time, which was postulated to result either from an increase in surface area or removal of a contaminant layer. Sun et al. explained the improved wettability of activated felts by the establishment of polar functional oxygen groups [4,12]. Zhong et al. suggested that wetting was improved by removing greasy residues from PAN-based felts after thermal activation at 400 °C for 30 h [16]. For a similar felt, Tham preferred activation at 650 °C for 4 h [20], whereas Smolinka suggested 400 °C for 20 h to be ideal [21].

The optimum activation conditions for one production charge is not necessarily the same for the next charge. From our own experience with PAN-based felt over many years, we have recognized some variability in the heating required to obtain the most favourable performance, which becomes obvious in terms of mass loss or by the wettability after the pre-treatment. To exemplify and investigate this observation two samples (A and B), identified by the graphite felt manufacturer as having been produced in different carbonisation and graphitisation runs, were used for this study. Whether the earlier stages leading to the formation of a felted PAN material differed is unknown to us.

2. Materials and methods

According to the supplier the felt (of type I PAN-based fibers) was a relatively high purity grade with charge A containing ~0.02% and B between 0.01% and 0.05% ash.

Due to the hydrophobicity of some test materials, felt samples were vacuum infiltrated with electrolyte to ensure a good contact between electrolyte and fibres. The felts were nominally 4.6 mm thick and cut into 30 × 30 mm² pieces. The samples were fixed on a non-porous, smooth graphite plate, which served as the current collector. A nitrogen purged 0.05 M aqueous solution of H₂SO₄ served as electrolyte. All electrochemical measurements were carried out and are reported with reference to a saturated Ag/AgCl electrode. Electrochemical double layer capacitance (EDLC) was calculated from the linear relationship between sweep rate and current in cyclic voltammograms (CV) recorded at 10 to 200 mV/s, in a voltage range where there was no evident redox reaction peak. Measurements of the EDLC and CVs were performed with an Arbin BT-2000 potentiostat.

Felts were oxidised in air in a Nabertherm (N60/65HA) oven to activate. The oven had previously been used exclusively for heating carbon felts and so may be considered effectively free of other

contaminants. The felt weight was measured with a Sartorius analytical balance (BP221S).

The morphology and fibre diameters of the felts were examined by scanning electron microscopy (FEGSEM, FEI Quanta 250F) using a 10 keV electron beam after mounting the samples onto aluminium stubs with conducting carbon adhesive tabs. The samples were not further prepared.

The bulk quality of both graphite felt (A and B) was characterized by x-ray diffraction (XRD) (X'Pert PRO, PANalytical, CuK α (Ni-filter) with Rietveld-analysis for 2 θ at peaks between 16–88°). Felts were measured after grinding to a fine powder with a pestle and mortar, together with a known amount of crystalline Al₂O₃ powder. The diffractogram allows a quantification of the ratio of both crystalline substances (graphite and Al₂O₃) and the crystal lattice parameters to be determined. Therefore, the amount of amorphous carbon could be estimated from the mismatch

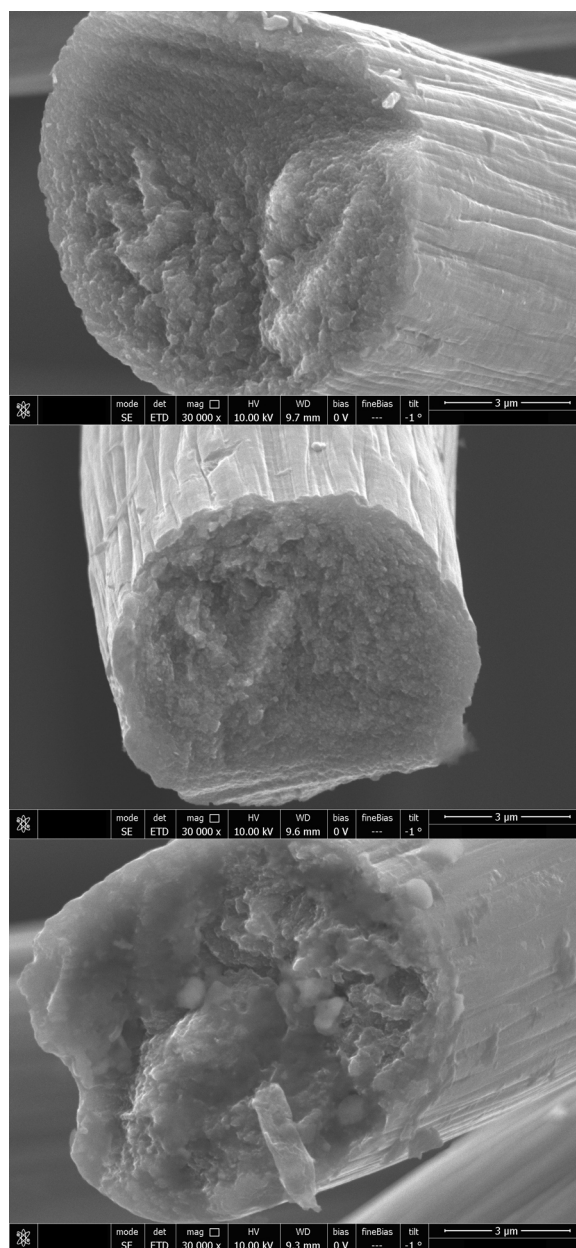


Fig. 1. Tips of untreated fibres from charge A (top) and charge B (middle), which showed evidence of tarry coatings on some fibres (bottom).

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