



Variability within a single type of polyacrylonitrile-based graphite felt after thermal treatment. Part II: chemical 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 part I of this study, 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. A difference due to bulk crystallinity or due to pronounced core-rim structures of the fibres has been excluded. In this second part a limitation from tarry coatings, which are a possible side products of graphitization, could not be corroborated. However, differences were ascribed to variations in the surface chemistry, which was characterised by Boehm method titration and cyclic voltammetry. The composition of the oxides is discussed together with the possible role they play in the activation and wetting of the felts. The rather high amount of oxides suggests that the Boehm method measures subsurface groups in addition to surface groups. The wetting quality of activated felts can be correlated well with the concentration of neutral quinone groups, characterised by cyclic voltammetry.

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1. Introduction

Graphite felts are suitable materials for use as electrodes in flow-through electrochemical reactors. However, the felts need to be properly activated in order to become hydrophilic and have low charge-transfer resistance. Among other techniques this is often undertaken by heating in air [1–4]. After heat treatment of many felts of one type from the same supplier under identical conditions we have often seen variability in the wettability and charge transfer resistance among different batches of graphite felt production (referred to as a production charge). This observation has led us to investigate the cause for these differences in more detail. It could be assumed that such strong variability has led other authors to try rather extreme conditions, like heating at 500 °C for up to 30 hours [1] or activation by refluxing in sulphuric acid, nitric acid and mixtures of both acids for up to 15 hours [5]. However, the short thermal treatment process investigated in this report is better suited to mass production.

The first part of this work [6] has shown that the felts taken from two production charges were similar in morphology and bulk physical characteristics as supplied. Despite this there were considerable differences during and after thermal activation. Charge B pitted, increased in electrochemical double-layer

capacitance (EDLC) and wettability at much lower temperatures than Charge A.

Charge B was also observed to have a patchy covering at single spots of what was possibly a tarry coating. Such deposits are known to condense during pyrolysis of PAN fibres and may redeposit on the felt. In this section the influence of the tarry coatings and the surface chemistry of the fibres is examined.

2. Materials and methods

Graphitic felts (PAN-based fibers type I, HM [7]) of high purity grade contained 0.02% ash (charge A) and between 0.01% and 0.05% (charge B). Felts were activated in air in a Nabertherm oven N60/65HA between 403–575 °C. The felt weight was measured with a Sartorius balance BP221S.

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. The felt samples were mounted in a purpose-built PVC holder (with an opening of 20 × 20 mm²), in which they were electrically connected to a smooth graphite contact plate by pressure only (the felt was compressed by ca. 20% in the holder). A N₂-purged 0.05 M aqueous solution of H₂SO₄ served as electrolyte. All electrochemical measurements were carried out and are

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reported with reference to a saturated Ag/AgCl electrode (Metrohm). EDLC was calculated from the linear relationship between sweep rate and current in CVs recorded at 10 to 200 mV/s, in a voltage range where there was no evident redox reaction peak. Measurements of the EDLC and cyclic voltammograms (CVs) were performed with an Arbin BT-2000 potentiostat.

The Boehm method was used to determine the coverage of acidic and basic groups. Specifically, suspensions of felts were prepared in 0.05 M NaOH (to determine acidic groups) or in 0.05 M HCl (for basic groups). Suspensions were prepared by cutting samples of the felt into small pieces (size of pieces 2×2 mm). After the reaction of ca. 1.7 g felt in 75 ml basic or acidic solution for 48 h under humidified nitrogen and permanent stirring, the suspension was filtered, through an inert filter [8] and washed with nitrogen purged deionised water. Thereafter 100 ml of HCl (0.05 M) or NaOH (0.05 M) were added and the resulting amount of acid and base were titrated with N_2 purged 0.05 M NaOH or 0.05 M HCl, respectively (pH measurement (pH-meter: WTW pH538) using a glass pH electrode (Mettler Toledo InLab Micro)). Contact with air was minimised, as far as possible, to prevent any influence from CO_2 . All Boehm experiments were performed with one blank acid or base sample (without felt) and showed no changes of concentration after the described procedure. All chemicals used were purum p.a. grade from the Sigma-Aldrich group.

3. Results & discussion

Considerable variations are observed between two PAN-based graphite charges after thermal activation. Both charges are samples of the same graphitization type from one supplier. To understand if these variations result from bulk or surface differences the basic material characteristics, crystalline bulk properties and the surface topography were examined in part I. However, there was no significant difference in the measured properties of the felt charges A and B as supplied.

3.1. Surface contamination

To find out whether the different behaviour is caused by variations of surface chemistry of the fibres itself or by an accidental influence due to dirt or other coatings felt samples have been cleaned with organic solvents before thermal activation. From the literature it is known that tarry compounds on fibres can be a side product during the graphitization. Shui et al. found that tarry coatings (polyaromatic hydrocarbons) on carbon filaments lead to reduced reversibility of a Fe^{2+}/Fe^{3+} redox couple and decreased electrochemical capacitance [9]. Furthermore they could show that cleaning the filaments with acetone or dichloromethane increased the capacitance by a factor of 4.6 and lead to reversible electrode reactions. Similar to the results of Shui, Zielke et al. found that the surface of carbon fibres can exhibit polyaromatic compounds from the graphitization [10]. These compounds have to be removed before further analysis, which was shown to be possible by careful extraction with methanol and even better boiling water. Nevertheless the processes of drying in air and subsequent treatment are reported to be very critical for the further investigations. From the SEM-images in part I, in few spots on the fibre surface of charge B an additional adhering layer was found, which were presumably tarry droplets. Although no droplets were seen on fibres of charge A some surface contamination may be anticipated.

Felt samples from charge A and B have been cleaned in an ultrasound bath with ethanol, acetone and dichloromethane and subsequently rinsed with the same solvents to test, whether a possible contamination is present which enhances or limits the mass loss during activation.

Treatment of felts from charge A with organic solvents and evaporation for 96 h in air at room temperature prior to thermal activation at $450^\circ C$ for 2 h, did not alter the wettability or EDLC, in comparison to a felt that was thermally activated without cleaning. The mass loss at $450^\circ C$ for 2 h was $<0.2\%$ for all felts, whether rinsed or not. Also the wettability for the cleaned felts still was hydrophobic after activation. Therefore, if there were tarry deposits on charge A, they did not have a significant influence on the thermal activation and do not limit the activation of felts.

If a contamination was responsible for the higher reactivity of charge B it could be expected that by cleaning the burn off becomes comparable to charge A ($<0.2\%$). After rinsing in all solvents and evaporation for 96 h at room temperature two samples of this charge showed a mass loss of 0.35% during activation at $450^\circ C$, which is significantly higher than for charge A and the wettability was very good. Therefore it can be concluded that charge B only contains very small amounts of contamination and is more reactive for other reasons.

However it can be shown that it is possible to clean felts by rinsing with organic solvents. Evidence for contamination on other charges of the same felt type (charge C), which are not subject to enquiry in the first part of this paper, have been found. In Fig. 1 the CVs show a distinct pair of peaks at around 0.3 V vs. Ag/AgCl on the same type of PAN-based graphite felt as received. The peaks separation was narrow at ca. 70 mV and the peaks roughly symmetrical, and returning to the background current after the peak. This would be expected for exhaustive electrolysis of a thin static layer of electroactive material. No peaks were visible after ultrasonication in ethanol (followed by 96 h drying in air at room temperature). This would imply that felt charge C was contaminated with a redox-active, ethanol soluble impurity. This is presumably an organic compound, although the nature of the contamination has not been analysed.

CVs of untreated charge A and B felts (given in Fig. 2 and Fig. 3) showed no anodic peak at $E = 0.3$ V, but a small and broad anodic peak at $E = 0.75$ V and a slight cathodic peak at 0.25 V, which has been observed on most charges. If these peaks correspond to the same redox couple then the reaction is irreversible at this sweep rate. The treatment with organic solvents lead to a small decrease of the capacitive currents (in contrast to the work of Shui and Fryszyk) and a slight shift in the peak height and peak position of this oxidation reaction. We attribute this peak to functional quinonoid groups, which may be native to the carbon surface. The decrease in EDLC and increase in the peak spacing after rinsing in organic

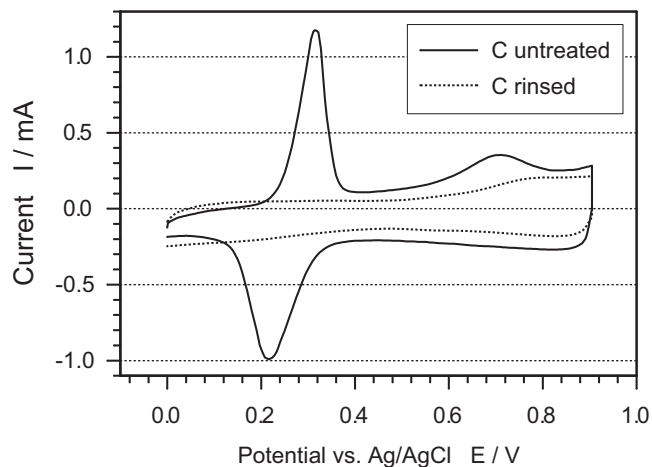


Fig. 1. CV (20 mV/s 0.05 M H_2SO_4) of felt from charge C as received (solid) and with ultrasonic cleaning in organic solvents (dashed). An ethanol soluble compound is detected by a redox pair at 0.3 V vs. Ag/AgCl for the sample as received.

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