



Performance evaluation of thermally treated graphite felt electrodes for vanadium redox flow battery and their four-point single cell characterization



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HIGHLIGHTS

- Effect of thermal treatment on graphite felt electrode performance was investigated.
- Results of cyclic voltammetry do not correlate with single-cell testing for cathode.
- Complex 4-point method for single-cell characterization was developed.
- Distribution of ohmic and faradaic losses in single-cell was evaluated.
- Kinetics of cathode reaction was found unaffected by oxygen functionalization.

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ABSTRACT

In our contribution we study the electrocatalytic effect of oxygen functionalization of thermally treated graphite felt on kinetics of electrode reactions of vanadium redox flow battery. Chemical and morphological changes of the felts are analysed by standard physico-chemical characterization techniques. A complex method four-point method is developed and employed for characterization of the felts in a laboratory single-cell. The method is based on electrochemical impedance spectroscopy and load curves measurements of positive and negative half-cells using platinum wire pseudo-reference electrodes. The distribution of ohmic and faradaic losses within a single-cell is evaluated for both symmetric and asymmetric electrode set-up with respect to the treatment conditions. Positive effect of oxygen functionalization is observed only for negative electrode, whereas kinetics of positive electrode reaction is almost unaffected by the treatment. This is in a contradiction to the results of typically employed cyclic voltammetric characterization which indicate that both electrodes are enhanced by the treatment to a similar extent. The developed four-point characterization method can be further used e.g., for the component screening and *in-situ* durability studies on single-cell scale redox flow batteries of various chemistries.

1. Introduction

The actual growth in the electricity production from the renewable energy sources operating in the intermittent regime (such as wind turbines and photovoltaic cells) emphasizes the need for flexible, cheap and reliable technology for large scale energy storage. Among various energy storage options the vanadium redox flow battery (VRFB) represents an interesting alternative. Comparing to classical static accumulators, the energy is stored in external tanks in the form of aqueous vanadium-based electrolytes which are circulated through the battery stack, where the energy conversion is associated with the electrochemical reactions of vanadium ions on inert electrodes. The VRFB

concept is schematically described in Supplementary data 1. The flow concept provides the battery with several advantageous features such as: i) decoupled power (kW) and capacity (kWh); ii) easy removal of waste heat; and iii) reduced self-discharge. Moreover, superior cyclability (over 10 000 cycles) is expected due to the absence of phase changes on the electrodes (e.g., metal deposition, gas evolution or ion intercalation) within the battery operation and a single electrochemically active element used in both, positive and negative, electrolytes. These features, together with reasonable efficiency of energy conversion (above 80% DC-DC) and fast response time (in tens of ms), predetermine the technology for stationary energy storage applications [1,2].

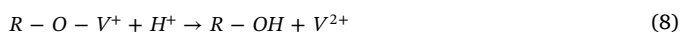
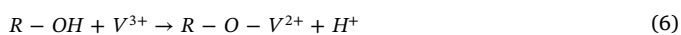
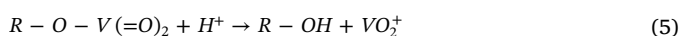
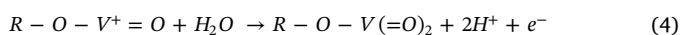
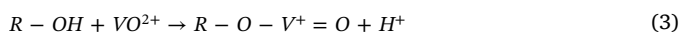
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The VRFB electrode reactions, together with the corresponding standard reduction potentials, are presented in the direction of reduction in eqs. (1) and (2).



The sluggish reaction kinetic of typically used graphite felt electrodes towards the VRFB electrode reactions is usually addressed by the heat treatment of the felts in the presence of air. The partial oxidation of the surface of graphite fibres by the oxygen contained in air increases the wettability of the originally rather hydrophobic graphitic material, which, in turn, increases the electrode-electrolyte interface area. At the same time, oxygen functional groups created on the fibre surface are believed to catalyse the VRFB electrochemical reactions [3]. The three-step reaction mechanism is usually used to describe the positive (eqs. (3)–(5)) and the negative (eqs. (6)–(8)) charging electrode reaction at hydroxylated carbon electrode [3]:



The specific optimal conditions of thermal activation are known to be strongly dependent on the overall history of the carbon electrode material including: choice of fibre precursor (rayon or polyacrylonitrile) [4], texture properties of the porous matrix (carbon felt or paper) [5], conditions of carbonization and graphitization [6] as well as the content of impurities [7]. Besides the apparent differences between various porous carbon materials, Rabbow et al. recently draw attention to the poor reproducibility of the thermal activation of the PAN-based felts [8,9]. For different charges of the same felt material significantly different effect of the same thermal activation procedure was observed with respect to mass losses, specific capacitance and content of oxygen functional groups. The oxidative effect of the thermal treatment can be also enhanced by the increase of oxygen concentration in the gas mixture [10], resulting in a significant improvement of performance of graphite paper electrodes as a consequence of the increased roughness of the fibres surface.

The electrochemical activity of carbon materials is known to be strongly related to the microstructure of the surface layer, more specifically to the content of the carbon edge sites and defects. According to Chu et al. [7] the gas-phase treatment of graphitic material increases the content of edge sites due to etching of the basal plane skin layer. According to Ehrburger et al. [6] the sensitivity of carbon materials towards the oxidation can be related to the so-called active surface area (ASA), which express the content of the catalytically active edge sites and defects of graphene sheets. This can be experimentally quantified by oxygen chemisorption followed by the measurements of carbon oxides evolved during the subsequent degassing at elevated temperatures.

Despite two decades which have passed since Sun et al. firstly reported on the thermal treatment of graphite felts for VRFB [11], the role of the oxygen functionalities on the electrochemical performance of the felt electrodes still seems to be rather controversial. The positive effect of the oxygen functionalities on the kinetics of the battery electrode reactions has been repeatedly reported in the past [4], [12–14]. However, contrary to that, the inhibiting effect of electrode surface oxidation on positive VRFB electrode reaction has been recently indicated by several papers [15–17]. Bourke et al. reported the negative effect of anodic polarization on the various amorphous and crystalline carbon

materials (including graphite fibres) on the kinetics of positive VRFB electrode reaction. Similar trends for the VO_2^+/VO^{2+} redox couples were observed by Friedl et al. who tested the effect of chemical functionalization of multi-walled carbon nanotubes [16]. Also Melke et al. reported negative effect of thermal treatment on electrode reaction kinetics for less graphitized carbons due to decreased content of sp^2 carbon atoms in the surface layer and related increased ohmic losses [17,18].

The discrepancy between these reports may originate in inappropriate experimental approaches which are typically employed for the evaluation of electrocatalytic activity of carbon-based electrodes towards the battery electrode reactions. Most of the publications in the field employ cyclic voltammetry (CV) measured in diluted vanadium electrolytes (as it is comprehensively reviewed in Ref. [19]), with the evaluation based on to the separation of oxidation and reduction peak potential. This is typically followed by a single-cell characterization in symmetric electrode set-up, i.e., with both positive and negative electrode being treated equally.

In our contribution, the relevancy of such characterization approach is critically assessed on a series of thermally treated graphite felt electrodes where the discrepancy between the results of CV and symmetric single-cell characterization is observed. Based on the results we propose a complex single-cell characterization method combining electrochemical impedance spectroscopy (EIS) and load curve (LC) measurements in 4-electrode set-up. The distribution of ohmic and faradaic losses of individual cell components within the single-cell is directly evaluated from these measurements. This enables us to study the effect of electrode functionalization of positive and negative electrode independently.

2. Experimental part

2.1. Thermal modification of graphite felts

Rayon-based graphite felt with the thickness of 5.0 mm and fibre diameter of approx. $10 \mu\text{m}$ was used within the study. The thermal treatment was conducted in electrical furnace under various temperatures (400, 450, 500, 550 and $600 \text{ }^\circ\text{C}$) for 9 h. The temperature was ramped with the $10 \text{ }^\circ\text{C min}^{-1}$ rate to a given temperature and after 9 h time period, it cooled down to room temperature spontaneously. The weight of felt before and after the treatment was measured using analytical laboratory scales.

2.2. Physical characterization of the felt

X-ray photoelectron spectroscopy (XPS) ESCAProbeP (Omicron Nanotechnology) and confocal DXR Raman microscope (ThermoFischer Scientific) were used to observe the changes of surface composition of the felt due to thermal treatment. Scanning electron microscope (SEM) VEGA3 (Tescan) was used to observe the morphological changes of the graphite fibres. Thermogravimetric analysis (TGA) using thermogravimetre Q 500 (TA Instruments) was used to characterize thermal stability of the felt under nitrogen, air and oxygen atmosphere. The specific surface area (SSA) of felts was measured by nitrogen adsorption at $-196.15 \text{ }^\circ\text{C}$ using 3Flex physisorption instrument (Micromeritics) and calculated from BET isotherms. Prior to the measurement, the sample was desorbed for 1000 min in vacuum at $105 \text{ }^\circ\text{C}$. The wettability of the felts was characterized by dropping of demineralized water on to the felt sample and classified in terms of wettability degrees, according to Rabbow et al. [8].

Through-plane area specific resistance (ASR) of graphite felt was measured by ohmmeter BS407 (Aim-TTi Instruments) in 4-probe setup with a measured felt sample surrounded by two pieces of commercial composite plate PPG86 (Eisenhuth). The felt resistance was measured at 25% compression of its initial thickness, which corresponds to the compression in our laboratory single-cell.

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