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Short communication

X-ray micro-tomography as a diagnostic tool for the electrode degradation in vanadium redox flow batteries

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ABSTRACT

Micro-tomography (CT) can be successfully employed to characterize ex situ the structural changes occurring in graphite felt electrodes during vanadium redox flow battery (VRFB) operation. Coupled high resolution X-ray and electron microscopy in conjunction with XPS are used to elucidate the microstructural and chemical changes to the high voltage RFB carbon electrode. The results reveal the onset of corrosion of the carbon felt structure relatively early in the VRFB life-cycle, extended operation is expected to result in extensive microstructural evolution effects.

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1. Introduction

The vanadium redox flow battery (VRFB) is an electrochemical device suitable for large-scale energy storage due to its fast response time, long cycle life, and high energy efficiency [1,2]. In VRFBs, the electrodes provide the sites to facilitate the redox reactions between V^{3+}/V^{2+} and V^{4+}/V^{5+} ions [2,3].

Graphite felt is the most common electrode material employed in VRFBs due to its low cost, high stability and conductivity, and reasonable surface area [4,5]. To improve the activity of the felt, several surface treatments have been employed to alter the felt surface chemistry and, consequently, to improve the reaction kinetics at the electrodes. These include thermal activation [6], chemical etching/doping [1,7], nitrogen doping [8] and functionalization of the surface with hydroxyl groups [9]. Recent publications demonstrate that substantial performance gains can be achieved with improved design of these felt materials [10–13].

Tomograms of fresh graphite felt have already been obtained and used to extract detailed structural characteristics of electrodes (surface area, porosity, fiber diameter and volume) [14,15]. Based on the acquired structural information, 3D pore scale models have been built to investigate the effect of electrolyte flow rate, vanadium ion concentration and electrode morphology on VRFB performance. It has been found that overall cell voltage can be enhanced by increasing flow rate and by employing denser electrode structure [14,15].

However, even though this model-based design approach has helped optimize the fresh felt material, pore scale models for VRFBs would be much more accurate and realistic if the structural information of used (voltage-cycled) felts were incorporated in the model to capture the changes in felt structure and properties during operation.

Using a combination of micro-tomography (CT) measurements of voltage-cycled graphite felts (over ca. 30 charge/discharge cycles), scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS) measurements of the same felt electrode, the first description of microstructural evolution processes occurring in VRFB felts during operation is provided in this paper.

2. Experimental

Graphite felts (Sigracell®; GFA6) were harvested from the positive electrode (V^{4+}/V^{5+}) of a VRFB in a ‘fresh’ and ‘used’ state — ‘fresh’ felts were thermally activated and had undergone compression identical to those used in working VRFBs. ‘Fresh’ felts were in contact with the electrolyte solution, but had not been electrochemically cycled, whereas the ‘used’ felts underwent 33 charge/discharge cycles (Fig. 3(D)). Vanadium (IV) oxide sulfate (hydrate, 97%) was used as the starting electrolyte solution. In order to prepare V^{2+} and V^{5+} ions, anolyte and catholyte were filled with 1:2 ratio of V(IV) solution (1.5 M in 3 M H_2SO_4) respectively and the required ions were obtained by charging of the VRB. The resulting solutions in anolyte and catholyte were 1.5 M V^{2+}/V^{3+} and 1.5 M VO^{2+}/VO_2^+ respectively, both in 3 M H_2SO_4 solution. Charge–discharge tests were conducted at a constant current density of 100 mA cm^{-2} at 30 °C. The cut-off voltages for the

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charge (upper limit) and discharge (lower limit) cycles were 1.65 and 0.65 V, respectively. The maximum cut-off voltage used during charging (1.65 V) was selected based on the maximum potential the battery could hold without excessive hydrogen evolution. The lower cut-off cell voltage during discharge (0.65 V) was selected to allow complete discharge of the battery.

Samples of 'fresh' and 'used' graphite felts were characterized in 3D using the micro-CT facility at the TOMCAT beamline at the Swiss Light Source. Using a parallel beam setup at 10.5 keV in absorption mode, 1500 projections were acquired for each tomographic scan during a 180° rotation with a radiation exposure time of 200 ms for each projection image, providing an effective pixel size of 0.65 μm. Tomographic reconstruction of the acquired projection images was performed using the Gridrec algorithm [16] after application of flat and dark field corrections. Image analysis of the raw data was performed using the Avizo Fire software package (FEI): for each acquired tomographic volume, a cubic region-of-interest (0.48 mm^3) was extracted for subsequent analysis, a smoothing filter was then applied to the grayscale image sequences for image de-noising; followed by a watershed segmentation to separate the solid phase (graphite fibers) from the pore phase, this is a well-established work-flow that has previously been applied to graphite materials [17].

3. Results and discussion

Cross-sections of the micro-tomograms of 'fresh' and voltage-cycled graphite felts are shown in Figs. 1(a) and 2(a). 'Fresh' graphite felt fibers have uniform density, whereas an alteration of the structure of the used voltage-cycled graphite felts is observed, this micro structural evolution is manifested as the appearance of agglomerated fiber bundles, and non-uniform density across individual fibers, consistent with electrochemical oxidation of the carbon structure.

The observed structural changes were verified by the 3D reconstructed images of graphite felt samples. 'Fresh' graphite felt (Fig. 1(B)) consists of individual fibers (fiber size ~ 13 μm) forming 'bundles' throughout its structure, whereas the voltage-cycled felt (Fig. 2(B)) structure is dominated by agglomerated fibers.

Key geometric characteristics of the graphite felt samples (porosity, volume specific surface area and characteristic tortuosity) can be extracted from the 3D reconstructed images. Tortuosity values were calculated using an established methodology in StarCCM$^+$ software (see [18]). A small decrease in the calculated porosity and increase in tortuosity values [18] is observed in the case of voltage-cycled graphite felt as a consequence of the charge/discharge cycling for a short period of time (~65 h). A small increase in the pore phase characteristic tortuosity of voltage-cycled electrode is observed due to the densification of the structure as a result of graphite felt oxidation. However, there is a significant reduction (~37%) in the volume specific surface area of the voltage-cycled graphite felt sample after 60 h of continuous VRFB testing, indicating its structural alteration due to carbon oxidation and fiber agglomeration (Table 1). BET was employed to experimentally verify the observed changes in surface area by CT. The BET surface area of the 'fresh' sample was 23 $m^2\,g^{-1}$ and it was reduced to 14 $m^2\,g^{-1}$ for the voltage cycled sample, indicating a similar reduction in the surface area of the voltage-cycled graphite felt sample. This significant change in the microstructure of the felt will influence the microscopic transport and reaction phenomena occurring in the electrode, and thereby affect device-level performance.

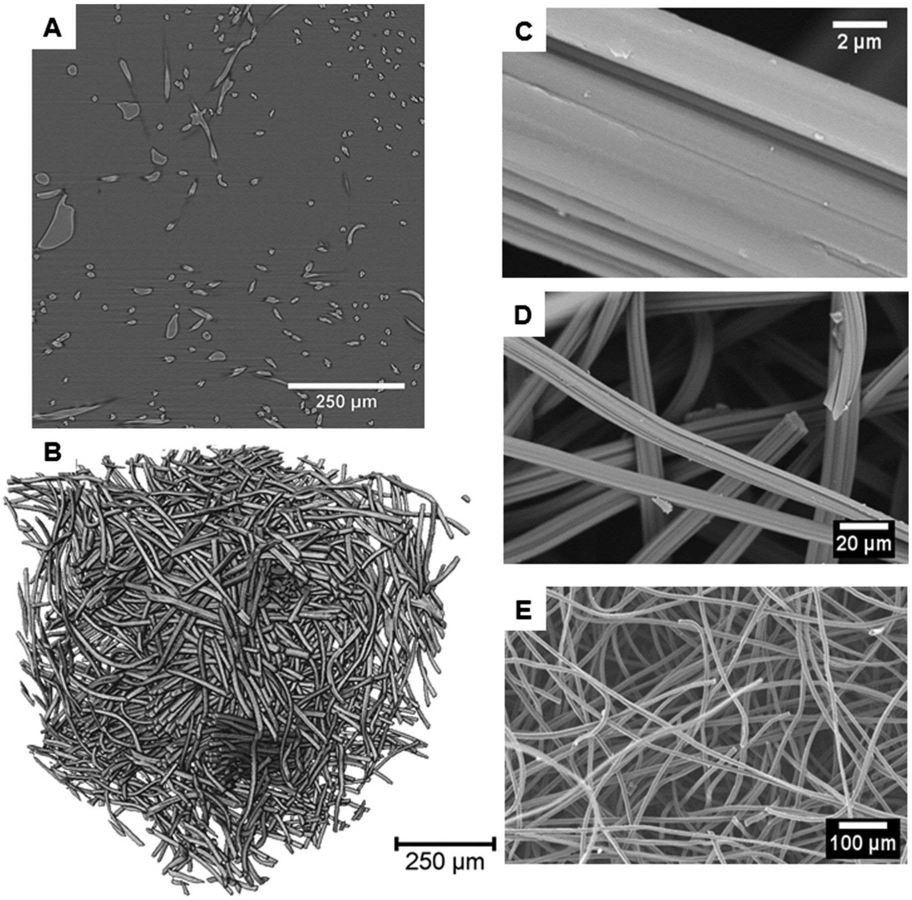

Fig. 1. A) Cross-section of the 'fresh' graphite felt electrode where the gray and dark gray regions represent the fibers and open pore structure respectively; B) 3D reconstructed image of the 'fresh' graphite felt electrode; c–e) SEM images of the 'fresh' graphite felt electrode.

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