Graphite-polypropylene bipolar plates (BPP) were subjected to galvanostatic treatment in highly charged positive and negative vanadium electrolyte solutions. The tests were performed in an ex-situ three-electrode electrochemical cell in order to simulate aging under harsh overcharging conditions in a vanadium redox flow battery (VRFB). Non-destructive computed microtomography (microCT) technique was employed to study the post aging morphological changes. The investigations revealed that even under massive hydrogen evolution conditions in the negative electrolyte the BPP is stable. However, the BPP suffers from intense corrosion associated with morphological deformations during aging by galvanostatic overcharging in the positive electrolyte. The CO/CO₂ gas evolution leads to formation of an open pore network, development of micro-cracks and meso-fractures. These morphological changes cause an expansion of the corroded bulk material. The results show that the corrosion starts at the electrolyte/BPP interface and propagates with time in plane-parallel direction to the back side of the BPP. © The Author(s) 2018. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.0921805jes]

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Energy storage systems are necessary in order to balance temporary mismatch times of oversupply and overdemand of electrical energy, especially in scenarios with a high ratio of intermittent renewable energy obtained from wind and solar power. Stationary rechargeable batteries, such as the vanadium redox flow battery (VRFB), represent one type of energy storage for that purpose. It can be designed in a stack-setup with the size of electrolyte tanks and reaction units adapted separately for different applications with various energy and power needs. An important component of the VRFB stack is the current collector, which is a carbon-based bipolar plate (BPP) electrically connecting and physically separating adjacent cells. The functionality of the BPP is achieved by combining conductive compounds such as graphite, carbon nanotubes and carbon blacks with binders like polyethylene, polypropylene, epoxy resin or fluoropolymers to form carbon composite materials. Due to the dense composite structure, the BPP hinders the electrolyte to cross bidirectional between adjacent positive (VO₂⁻/V⁴⁺⁻) and negative (V²⁺⁺/V⁻⁻) half-cells. In order to maintain the impermeability of the BPPs and the performance of the whole VRFB, the BPPs need to be (electro-)chemically resistant to the vanadium electrolyte solution to prevent corrosion and the subsequent formation of leakage paths. However, the half-cell electrolytes reach high states of charge (SOC) and at the same time the potential increases while the battery is charged. The rate of side reactions such as gas evolution of H₂ and O₂, CO and CO₂ increases at high SOC in combination with high potentials and can cause irreversible aging effects. Several ex-situ approaches were carried out in order to study the aging of carbon compound BPPs in an electrochemical three-electrode cell setup. Appearance of oxygen functional groups on the surface of carbon-polyethylene compound BPPs and beginning delamination processes occurred after applying a polarization potential of 2.5 V vs. SCE for 6 h in 2 M VOSO₄ in 2 M H₂SO₄ electrolyte solution. In conjunction with delamination, the formation of micro-cracks and an increase in through-plane resistance were observed for a carbon-graphite composite BPP which was treated at 1.6 V and 200 A/m² in a vanadium electrolyte containing 2.1 M VO²⁺. In different approaches the X-ray computed microtomography (microCT) turned out to be a useful method for visualizing and quantitatively analyzing structural damages in materials. The development of pores and cracks as well as their orientation can be well investigated. The main advantage of microCT is the non-invasive and non-destructive study of materials with high resolution images in 3D orientation.

In former contributions we have investigated the chemical and cycling stability of injection-moulded graphite-polypropylene composite BPPs in the VRFB electrolyte. The calendar aging method showed that the BPPs have a high chemical stability and only the surface of the BPPs in the positive electrolyte was oxidized while no morphological changes or loss in conductivity could be observed. On the other hand, the galvanodynamic cycling experiment at different SOC in the positive vanadium electrolyte revealed commencing morphological alteration due to graphite corrosion resulting in an increase of open porosity in the topmost bulk region of the BPP - especially at high SOC. The observations led to the question how overcharging conditions in a VRFB would affect the BPP. Therefore, we focus in this work on ex-situ galvanostatic aging of injection-moulded graphite-polypropylene BPPs in the positive as well as the negative VRFB half-cell electrolyte at high SOC. For this purpose, a three-electrode electrochemical cell was used in order to simulate overcharging conditions in a VRFB. Qualitative and quantitative microCT evaluation was performed as main analytical method in order to investigate the morphological deformations of the BPP samples as function of aging time. To the best of our knowledge, there is no systematic study about the corrosion stages and effects of BPPs that were subjected to overcharging conditions in the VRFB. According to the authors’ knowledge, especially the impact of overcharging conditions on BPPs in the negative electrolyte was not examined elsewhere.

**Experimental**

**Sample pretreatment.**—The BPPs with a thickness of 1.5 mm are composed of 86% graphite and 14% polypropylene and prepared by injection-moulding and subsequent sandblasting (PPG86, Eisenhuth GmbH & Co. KG, Germany). The samples were cut into round disks of 16 mm diameter. Before electrochemical aging, all BPP samples were cleaned by successive immersion in deionized water, ethanol and acetone for 15 min each and then in deionized water again for 30 min.

**Electrolyte preparation.**—The vanadium electrolyte (Oxkem Limited, United Kingdom, nominal ratio of 51:49, V⁵⁺⁻/VO₂⁻⁻) consists of 1.6 mol/L V⁵⁺⁻ in 2.1 mol/L H₂SO₄. The SOC of the positive and the negative electrolyte was adjusted to 90% SOC (approximately 10% VO₂⁻⁻/90% VO₂⁻⁻ and 10% V²⁺⁺/90% V²⁺⁺, respectively) by applying the required calculated electric charge in a VRFB single cell.
using a potentiostat/galvanostat (Solartron Analytical Modulab Pstat potentiostat/galvanostat, UK). The SOC value of (90 ± 3)% was rechecked by measuring the concentration of vanadium ions by means of UV/Vis spectrophotometry (LAMBDA XLS+, PerkinElmer, USA).15,16

**Aging of BPPs.**—The ex-situ aging of the BPPs was carried out in a conventional three-electrode electrochemical cell, placed inside a Faraday cage and recorded with a Pstat potentiostat/galvanostat (Solartron Analytical Modulab, UK). The BPP was connected as working electrode by exposing a geometrical surface area of 1 cm² to the electrolyte using a polypropylene sample holder with a poly(tetrafluoroethylene) seal (Metrohm Autolab B.V., Netherlands). A heat treated graphite felt (400 °C in air for 18 h, GFDS5; SGL Carbon Group, Germany) attached to a platinum wire served as counter electrode. The Hg/Hg2SO4 (+0.65 V vs. SHE) reference electrode was connected to the cell by a Luggin capillary. All potentials in this paper are quoted with respect to SHE if not indicated otherwise. The prepared positive and negative vanadium electrolytes (65 mL) with SOC 90% were used at room temperature (~22 °C) as electrolyte solutions. Prior to the measurements, the vanadium electrolyte was flushed with N2 for 15 min in the electrochemical cell and the inert atmosphere was maintained during the measurements. Galvanostatic aging was performed with current densities of 100 mA/cm² in the positive electrolyte and −100 mA/cm² in the negative electrolyte over different time periods. O2/CO/CO2 or H2 gas evolution as side reactions at the BPP working electrode reduced the SOC at most from 90% to 82% as checked by UV/Vis spectrophotometry after a 5 h aging test in the negative electrolyte. Even at this slightly reduced SOC the test resembles harsh overcharging condition at the used current density. This is also confirmed by the potential-time traces in Figure 1.

**Electrochemical analysis.**—The electrochemical behavior of the pristine and aged BPPs was investigated in 0.1 M H2SO4 electrolyte solution (Fisher Scientific, UK) in a three-electrode electrochemical cell. Cyclic voltammetry (CV) was recorded with a scan rate of 5 mV s⁻¹ between 0 V and 1.2 V. The double layer capacitance (Cdl; [F]) of the BPPs was estimated from the current at potentials, for which no pseudo-capacitive or faradaic contributions were visible in the CVs (i.e. 0.2 V for the aged samples and at 1.0 V for the pristine sample). The cathodic charge (Q; [C]) of quinone/hydroquinone functionalities was calculated by integration of the associated redox peaks of the CVs between 0.25 V and 0.65 V.

**Confocal microscopy.**—The surface roughness of the BPPs was measured by means of confocal microscopy (Sensofar, PLu neox, Spain). Ten different scans with the size of 127×127 μm² were selected from top to bottom of the BPPs. The VOIs were segmented into black/white 3D images with the software tool TauFactor in MATLAB (Version R2017a, MathWorks, USA) in order to calculate the relative diffusivity of the electrolyte through the pore phase along the z axis.

\[
\frac{D_{eff}}{D_i} = \frac{\varepsilon}{\tau}
\]

D_{eff} is the effective diffusivity through a porous volume; D_i is the intrinsic diffusivity coefficient of the vanadium electrolyte; \varepsilon is the volume of the porous phase; \tau is the tortuosity factor.

**Results and Discussion**

Graphite-polypropylene based BPPs were subjected to simulated harsh overcharging conditions in the negative and positive electrolyte of a VRFB performed in a three-electrode electrochemical cell. First, the negative vanadium electrolyte with SOC 90% was used and a current density of −100 mA/cm² was applied for 300 min. During the galvanostatic aging, negative potentials below −1.0 V vs. SHE were reached (Figure 1a). The noisy behavior of the potential response could be a result of H2 gas evolution that was observed during aging in good agreement with literature.17 In order to investigate the effect of gas evolution on the morphology of the BPP, samples were analyzed before (Figures 2a, 2d, 2g) and after (Figures 2b, 2e, 2h) the aging procedure by means of SEM, confocal microscopy and microCT. The pristine sample shows a rough but homogeneous surface with Sq of 4.1 μm. Although the surface roughness after aging in the negative electrolyte did not change significantly, the microCT image shows a slightly altered morphometric pattern of the surface area.
Figure 2. (a,b,c) SEM, (d,e,f) confocal microscopy and (g,h,i) microCT images of pristine BPP and BPPs that were aged in negative vanadium electrolyte with SOC 90% using a current density of $-100 \text{ mA/cm}^2$ for 300 min and in positive vanadium electrolyte with SOC 90% using a current density of 100 mA/cm$^2$ for 60 min.

shaped dents are visible at the top. This morphology change could be developed due to the observed gas evolution, while single particles could mechanically break off from the BPP surface. However, the 3D analysis gives no evidence for morphological changes in deeper regions. Due to the hydrophobic nature of the BPP, the electrolyte cannot penetrate into the BPP structure. Therefore, the BPP does not show indication of swelling and the gas evolution did not cause damage to the bulk material even after 300 min of galvanostatic treatment. As the observed differences of the BPP are rather negligible the graphite-polypropylene composite material can be considered as stable in the negative electrolyte even at harsh overcharging conditions.

A comparable investigation of overcharging conditions was performed in the positive vanadium electrolyte with SOC 90% by applying a galvanostatic current density of 100 mA/cm$^2$ for 60 min. During the aging procedure, potentials above 2.0 V vs. SHE were reached (Figure 1b). The repeated raise and decrease of potential response is most probably influenced by the evolution of CO, CO$_2$ and/or O$_2$ gas. In contrast to the aging in the negative electrolyte, the occurring gas evolution in the positive electrolyte caused morphological damage to the graphite-based BPPs (Figures 2c, 2f, 2i). The SEM image indicates a rougher surface compared to the pristine sample which is verified by the increase of Sq from $(4.1 \pm 0.6) \mu$m to $(7.9 \pm 2.7) \mu$m as measured by confocal microscopy. However, the main extent of the corrosion becomes apparent by examining the aged BPP by means of microCT. The 3D images provide clear evidence that the corrosion affects not only the BPP surface, but propagates into the bulk material, where cracks and an increasingly porous structure develop leading to a volume expansion of the BPP.

In order to investigate the progress of corrosion in the positive electrolyte with time, graphite-polypropylene BPPs were subjected to galvanostatic aging at the same current density of 100 mA/cm$^2$ for different durations (1, 10, 30, 60 and 180 min). All BPPs showed similar potential-time traces (Figure 1b). The BPPs exhibit capacitive behavior within the studied potential window in 0.1 M H$_2$SO$_4$ and it is apparent that the double layer capacitance $C_{dl}$ is rising with aging time (Figure 3). Moreover, a pseudo-capacitance at about 0.6 V vs. SHE can be observed which is attributed to the redox activity of quinone/hydroquinone (carbonyl and hydroxyl groups) on the surface of graphite particles. Thus, the associated charge $Q$ of the pseudo-capacitance is directly related to the amount of quinone/hydroquinone functionalities and is an indication for the degree of surface oxidation of the BPP. For better assessment of the changes that were induced by the overcharging experiments,
the charge $Q$ of the quinone/hydroquinone redox features as well as $C_{dl}$ were evaluated for each BPP and plotted as function of the aging time (Figure 4). For overcharging times up to 10 min the quinone/hydroquinone redox $Q$ rises with aging time. However, for longer overcharging times, $Q$ decreases. The decrease of $Q$ suggests further oxidation of the keto- and hydroxyl-groups to other oxygen-containing functional groups or even to CO/CO$_2$ gas. In contrary, $C_{dl}$ rises continuously with aging time. The presence of new oxygen-containing functional groups most likely increases the hydrophilicity of the BPP surface and promotes the wetting of a larger fraction of the internal surface, thus increasing $C_{dl}$ (Figure 4). In addition, the observed time-course of $C_{dl}$ is in agreement with an increase of the electrolyte/BPP interface due to surface roughening and electrolyte penetration into the BPP bulk. The CV is tilted and shows an increasingly resistive behavior with prolonged aging. The resulting shape of the CV after long aging could be attributed to the disruption of electrical conduction paths and/or to an increase of the internal electrolyte migration resistance due to significant morphological changes.\textsuperscript{20}

As the electrochemical data pose questions regarding the morphological changes of the BPP bulk structure, detailed quantitative evaluation and qualitative examination of microCT images were performed after the different aging periods. The diagram in Figure 5 shows the development of the open porosity in the bulk of the BPP. The zero point on the $x$-axis is set to the back side of the BPP since the front surface was subjected to aging in the electrolyte and is changing with treatment duration. The bulk of the pristine sample shows a very low open porosity with values $< 0.5\%$. At the front and back side, it has narrow regions with high open porosity due to the surface roughness.

On the other hand, the galvanostatically treated BPPs show an increase in open porosity at the front side in addition to a rising thickness of the corroded bulk as a function of aging time (Figure 5, Figure 6). High overpotentials cause oxidation of the graphite at the surface and in the flat bulk region. This also leads to CO and CO$_2$ evolution from side reactions.\textsuperscript{9,10} Thus, a significant increase in surface roughness with $S_q (7.0 \pm 1.3) \mu m$ in comparison to the pristine sample with $S_q (4.1 \pm 0.6) \mu m$ is already apparent after 10 min of treatment. In addition, the composite material becomes more hydrophilic due to the surface functional groups.\textsuperscript{15} Thus, the electrolyte can creep through the narrow open pore channels into the dense bulk material and causes growth of new open pore channels and coalescence of closed voids which further change the microstructure of the composite material.\textsuperscript{16} However, it is apparent that the intact bulk material of the aged BPPs diminishes rather slowly, while the thickness of corroded bulk material expands comparatively fast (Figure 6).

Therefore, a detailed qualitative examination of the 3D image from the non-destructive microCT measurement of the BPP treated for 180 min was performed in order to uncover the different extent of damage at the near-surface regions in contrast to the damage observed in the bulk of the BPP up to the border close to the intact bulk material (Figure 7). First, it is striking that meso-cracks (length dimension $L \approx 10^{-3} m$)\textsuperscript{21} are visible on the surface that enable the electrolyte to penetrate more easily into the BPP bulk. Moreover, the corroded bulk is also littered with micro-cracks (length dimension $L \approx 10^{-6} m$)\textsuperscript{21} which are very different from the dense and rather homogeneous structure of a pristine BPP. The heterogeneously distributed deformations at the microstructural scale might be initiated by local rupture and internal stresses due to mechanical anisotropy through different elastic and plastic properties at the graphite-polypropylene interface of the composite matrix.\textsuperscript{13} The formation of cracks might be benefited by pre-existing closed or open pores. In the corroded bulk structure the
micro-cracks are bridged by composite material. When the pressure of the accumulating gas in the corroded bulk structure exceeds the maximum tensile strength of the bridging material, it will start to break. Consequently, BPP fragments were found in the electrolyte solution that indicate loss of composite material. In addition, the breakings can lead to large fractures within the composite structure. This type of fracture is prominently visible in Figure 7 in the center of the corroded region. It is also reflected by a successive increase and decrease in open porosity from the surface to the end of the corroded bulk material in Figure 5. Therefore, the changes in the micro- and meso-structure in terms of cracks, fractures and mechanical breakages cause an expansion of composite material and thus have the strongest influence on the aging of the samples. The cracks and fractures show an anisotropic orientation rather parallel to the back side of the BPP. The fragile corroded material tears open more easily in horizontal direction than vertical into the intact bulk material which is therefore rather protected by its dense and strong composite matrix. Maybe the orientation of the particles in the production flow direction of the injection moulded BPPs could influence the corrosion development and thus the formation of horizontal cracks. However, the microCT image shows that the corrosion proceeds still further toward the intact bulk material by the slowly creeping electrolyte. The microCT 2D slices unravel that the

Figure 8. Schematic 2D overview of the proposed aging mechanism in graphite-polypropylene BPPs during harsh galvanostatic overcharging in positive vanadium electrolyte. (a) BPP surface at BPP/electrolyte interface is oxidized and becomes rougher due to CO$_2$/CO gas evolution which results in increasing hydrophilicity (symbolized by the water contact angle in the insets). (b) CO$_2$/CO gas evolution leads to larger open pore channel system and development of micro-cracks cause expansion of thickness of corroded BPP material. The corrosion front is creeping plane-parallel toward the back side of the BPP. (c) Diffusion limitations of electrolyte within the open pore structure lead to raise of side reactions. The development of meso-cracks and fractures is a result of mechanical breaking of bridging composite material due to accumulating gas in the corroded bulk structure. Single BPP particles are disrupted from the electrical conduction path. Legend: (1) BPP, (2) positive vanadium electrolyte with SOC 90%, (3) water contact angle on hydrophobic BPP surface, (4) water contact angle on hydrophilic BPP surface, (5) CO/CO$_2$/O$_2$ gas evolution, (6) closed pores, (7) open pores and micro-cracks, (8) bridging BPP material, (9) gas accumulation, (10) meso-cracks/fractures, (11) electrically disconnected BPP material.
creasing turns out to progress plane-parallel to the back side of the sample (Figure 7). A schematic overview of the proceeding corrosion and aging mechanism is summarized in Figure 8.

The morphological deformations, such as higher open porosity, cracks and breakages provide more options for electrochemical attack due to a larger effective electrolyte/BPP interface. Therefore, the main corrosion effects are probably affecting the already damaged region. Due to the same morphological deformations, however, some composite particles are detached from the electrical conduction path of the BPP working electrode matrix and therefore lose the potential to take part in the side reactions in good agreement with the observed increasingly resistive electrochemical behavior (Figure 3). Breakings and expansion of BPPs during overcharging conditions of an operated VRFB in situ could have impact on the compression of single battery components such as graphite felts or membranes. In addition, the matrix cracking and other microstructural deteriorations could reduce the mechanical strength and the lifetime of the BPP and lead to operation failure. In order to estimate the permeability of the corroded BPPs, possible electrolyte leaking paths through the bulk material of the most corroded BPP after 300 min of aging were analyzed via calculation of the diffusivity. The intrinsic diffusivity coefficient \( D_i \) of the redox couple \( \text{VO}_2^{+}/\text{VO}_2^{2+} \) ranges from \( 7.75 \times 10^{-8} \) up to \( 6.81 \times 10^{-10} \text{ m}^2\text{s}^{-1} \) extracted from literature examples.28–29 However, in the following analysis the relative diffusivity (\( D_{\text{rel}}(D_i) \)), ranging from values between 0–1, will be reported instead of the absolute values in order to highlight the impact of the microstructure on diffusive transport (Figure 9). The calculation uses the tortuosity factor \( \tau \) obtained from the microCT images. The tortuosity factor describes how convolutions and constrictions in the pore network affect the diffusivity. In the front region of the BPP, where the overcharging caused corrosion, \( \tau \) is low due to the wide open space in the fractured composite matrix. Therefore, \( D_{\text{rel}}(D_i) \) is high in this region and so the electrolyte can diffuse more easily through the fragile corroded structure. In contrast, the intact composite bulk material has comparatively narrow and only few open pore channels in \( \mu \text{m} \) scale with a high \( \tau \) value which results in very low relative diffusivity (\( D_{\text{rel}}(D_i) \sim 0 \)). The transition between high and low \( D_{\text{rel}}(D_i) \) takes place abruptly in good agreement with the microCT images which indicate a plane-parallel corrosion front creeping toward the back side of the BPP. Therefore, the composite BPP remains impervious for electrolyte leakages despite the application of very harsh overcharging conditions on the BPP in the positive electrolyte and observation of morphological defects. However, it might be possible that the BPP shows corrosion effects which would be more concentrated at some regions with higher overpotential during in situ overcharging operation of a VRFB stack than in other parts. Regions with higher overpotentials may preferentially develop leaking paths.

**Conclusions**

Graphite-polypropylene BPPs were aged in the highly charged negative and positive vanadium electrolytes in an ex-situ electrochemical three-electrode cell at high current densities in order to simulate harsh overcharging conditions. Although the galvanostatic treatment at \( \sim 100 \text{ mA/cm}^2 \) in the negative electrolyte for 300 min led to massive \( \text{H}_2 \) evolution, the impact of morphological damage is negligible and therefore the BPPs are rather stable in the negative electrolyte even under harsh conditions. In contrary, the BPPs suffer from corrosion and damage after overcharging in the positive electrolyte using \( 100 \text{ mA/cm}^2 \). The aging begins with an oxidation of the surface which was observed through the quinone/hydroquinone redox activity in the CV. Due to the new oxygen-containing functional groups, the surface becomes probably more hydrophilic and the electrolyte can creep into the narrow open pore system of the composite material near the surface. When the oxidation proceeds at high overpotentials, the carbon starts to erode and gas evolution of CO and \( \text{CO}_2 \) occurs. The subsequent expansion of the open pore system and the formation of micro-cracks provide larger electrolyte flow channels directed to the bulk of the BPP. When the bridging material between the micro-cracks starts to break due to the pressure of accumulating gas in the voids of the composite matrix, meso-cracks are formed and material is lost from the composite. The cracks are oriented parallel to the electrolyte/BPP interface in depth and increase faster than the advancement of the corrosion front toward the back side. The morphological deformations cause an expansion of the corroded BPP bulk. Despite the harsh overcharging conditions, the BPP remains impervious for electrolyte leakage due to the slowly proceeding creeping attack on the intact bulk material under the studied conditions. Nevertheless operation at overcharging conditions in the VRFB should be avoided in order to reduce possible corrosion effects. Further VRFB in situ investigations are necessary in order to study if hetrogeneously distributed overpotentials on the BPP surface could cause faster local corrosion with an associated accelerated formation of leakage paths between adjacent cells in the reaction unit.

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**ORCID**

Barbara Satola https://orcid.org/0000-0002-5807-1763
Gunter Wittstock https://orcid.org/0000-0002-6884-5515

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