

# Recent Progress in our Understanding of the Degradation of Carbon-Based Electrodes in Vanadium Redox Flow Batteries – Current Status and Next Steps

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This mini-review summarises and discusses recent findings from the literature on the degradation of carbon-based electrodes for vanadium redox flow batteries (VRFBs). It becomes evident that the focus of current investigations is on carbon paper, carbon felt and graphite felt electrodes, which is understandable from a practical point of view. However, the structural complexity of these materials often prohibits doubtless attribution of observed performance reduction (or increase) to changes in the electrode materials. Among the discussed major causes for degradation are formation or change of surface functional groups, changes in the carbon  $sp^2/sp^3$  ratio,

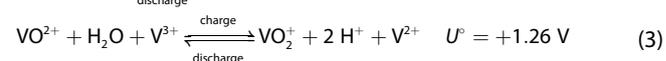
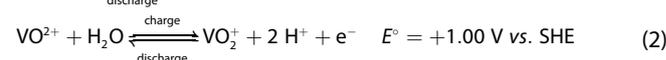
intercalation of ions as well as formation of inhibiting adsorbates. In order to gain deeper insight into the changes of carbon electrodes in VRFBs under relevant operation conditions, the authors suggest reducing complexity of the investigated materials and applying *in situ*-studies under well-defined and controllable conditions on model electrodes. These studies then should be extended towards more practical systems and may finally help to reduce degradation phenomena including enhanced overvoltages and thus could improve cycling and energy efficiency as well as long-term stability of vanadium redox flow batteries.

## 1. Introduction

The proceeding climate change, driven by the combustion of fossil fuels, is forcing a transformation in the energy supply of the continuously growing world population. Renewable energies are of fundamental importance to achieve this transition. Their advantages include, amongst others, a quasi-endless and geographically unlimited availability. Nevertheless, solar and wind energy, which are the renewable energies with the highest growth rates, are weather-dependent and thus their energy supply is unpredictable on a medium to long time scale. Therefore, storage systems are needed to stabilise the power grid in case of a deficit in supply. Besides electrolysis to produce hydrogen, electrochemical energy storage systems (ESSs), such as lithium-ion or redox flow batteries (RFBs), are considered a promising approach, as they offer an efficient, flexible and scalable way to store electrical energy.<sup>[1]</sup>

RFBs are characterised by the fact that the energy is stored in redox pairs dissolved in the electrolyte solutions, whereas the electrodes have a catalytic function and do not undergo any redox reactions during charging and discharging. In this way, in contrast to other ESSs, the energy density of RFBs can be scaled independently of the power density, which is a major advantage in addition to the comparatively low cost<sup>[2]</sup> and the fast

response time.<sup>[3]</sup> These advantages clearly outweigh the often-mentioned disadvantage of a generally low energy density, which, however, is not an issue for stationary applications. All-vanadium redox flow batteries (VRFBs), which contain the same electrochemically active element in both half-cells, have proven to be promising and have already been commercialised since several years.<sup>[4]</sup> The individual half-cell reactions taking place during charging and discharging as well as the associated standard electrode potentials  $E^\circ$  are shown in equations 1 and 2. Equation 3 additionally shows the overall reaction of VRFBs including the resulting standard cell voltage  $U^\circ$ .



The individual characteristics of VRFBs as well as the importance and development of the respective cell components have already been discussed in several review articles.<sup>[5]</sup> In addition to investigations on the electrolyte solutions<sup>[6]</sup> and the ion exchange membranes,<sup>[7]</sup> the used electrode materials are highly relevant, as they catalyse the above-mentioned electrochemical reactions (see equations 1 and 2). In particular, carbon-based electrodes are the established materials, as they are known for their good electrical conductivity, high chemical stability and reasonable cost.<sup>[8]</sup> Usually, the focus of research in this area lies on an increased performance and the development of efficient electrocatalysts, where recent developments are summarised in Refs. [8–10].

Theoretically, the number of charge and discharge cycles of VRFBs is unlimited, resulting in a long calendar lifetime (over

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10 years).<sup>[11]</sup> As mentioned above, compared to solid-phase systems such as lithium-ion or lead-acid batteries, the electrolyte solutions form the electrochemically active phase in VRFBs instead of the electrodes. Therefore, undesirable structural and morphological changes and the resulting mechanical stress on the electrodes during charging and discharging are avoided.<sup>[12]</sup> However, the quite harsh reaction conditions, such as the acidic environment ( $\text{H}_2\text{SO}_4$  as supporting electrolyte,  $\text{pH} < 1$ ) as well as the strongly oxidising ( $\text{VO}_2^+$ ) and reducing ( $\text{V}^{2+}$ ) ions have to be taken into account.<sup>[13]</sup> Degradation of the carbon-based electrodes may lead to poor kinetics of the redox reactions, enhanced overpotentials and thus reduced energy efficiency and battery capacity. Additionally, when considering the electrode potentials (see equations 1 and 2) and the given reaction conditions, it becomes evident that hydrogen and oxygen evolution must be considered as parasitic side reactions, especially during high charging currents and thus high overpotentials. These factors limit the lifespan of VRFBs and its carbon-based electrodes, in particular over an extended utilisation period.<sup>[13]</sup> But in terms of a reliable and economical operation, the long-term stability of the individual cell components is of great importance.<sup>[4]</sup> Future progress in this field requires precise knowledge of the involved degradation mechanisms to develop durable materials. Nonetheless, there is only a small number of publications dealing with this topic, while YUAN et al. summarised the state of knowledge up to 2019 in a review article.<sup>[1]</sup> Here the effects of long-term cycling on the performance of VRFBs, including mitigation strategies, are described, discussing the most important cell components, such as electrolyte, membrane, electrode and bipolar plate.

The investigation of degradation mechanisms is quite complex, as many different processes may occur. These individual contributions first have to be separated from each other in order to be able to evaluate their influence on the performance, since not every change in the electrode (surface) structure is necessarily adverse to performance. In this regard, a prominent example is the presence of surface oxygen functional groups, which may be introduced on purpose (see Chapter 2) or form during operation by surface oxidation. These groups have either been said to enhance redox activity of the electrode by forming active sites<sup>[14,15]</sup> or by improved

hydrophilicity,<sup>[16]</sup> but were also shown to serve as adsorption sites for different vanadium species leading to blocking of redox active sites, depending on the catalysed half-cell reaction (i.e., equation 1 or 2).<sup>[17]</sup> An in-depth understanding of such phenomena is essential for the design of new, long-lasting materials. In particular, the structural and chemical heterogeneity of carbon-based electrodes<sup>[13]</sup> often complicates such a knowledge-based approach, which might be one reason for the limited number of publications in this field. This mini-review is supposed to give condensed insight into the current state of knowledge regarding the degradation of carbon-based electrodes in VRFBs. In addition to changes in the electrochemical activity, the focus will be on structural transformations that are caused by long-term use and thus influence the overall performance. Finally, possible approaches for targeted investigations of the contributing factors will be given in form of an outlook.

## 2. Degradation of Carbon-based Electrodes in VRFBs

As a key component in RFBs, the electrodes provide the active sites for the desired electrochemical conversions. With regard to VRFBs, carbon-based materials, such as graphite felt (GF), carbon felt (CF), carbon paper (CP) and carbon cloth (CC) are common,<sup>[8,18]</sup> although pre-treatment is usually necessary to ensure sufficient activity and reversibility towards the conversion of the different vanadium species (see equations 1 and 2). In a recent review article, He et al. have summarised the possibilities in this field, including the introduction of metallic or carbon-based active components.<sup>[9]</sup>

However, as already mentioned, in addition to these activity considerations, degradation phenomena, especially under fluctuating conditions, must always be taken into account for a long-life operation. Various issues, like thermally, mechanically, chemically or electrochemically induced changes, can be identified as possible causes for alterations in performance.<sup>[19]</sup> Chemical degradation summarises all processes that take place under electroless conditions, i.e. through reactions with the



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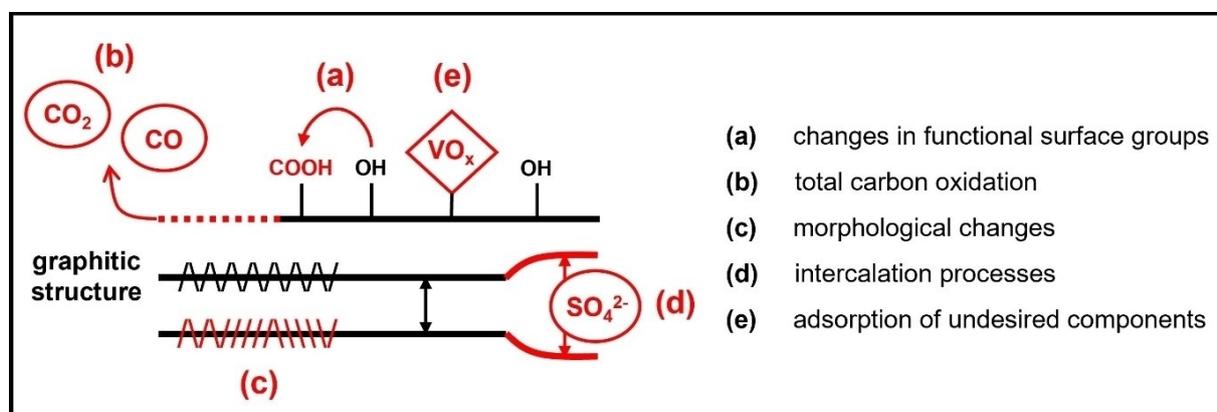
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components of the electrolyte solutions (e.g.  $\text{H}_2\text{SO}_4$  and/or vanadium species). Thus, for example, a change in the carbon-based surface through oxidation or the formation of different adsorbates are possible, which can significantly alter the materials properties. On the other hand, electrochemical degradation recognises the stability in the operating potential range and includes phenomena such as parasitic side reactions, which can affect the overall performance of VRFBs and damage the electrode. In the negative half-cell ( $\text{V}^{2+}/\text{V}^{3+}$ ), the hydrogen evolution reaction (HER) is a relevant side reaction, whereas in the positive half-cell ( $\text{VO}^{2+}/\text{VO}_2^+$ ), oxygen evolution reaction (OER) and the oxidation of the carbon-based electrode, also known as carbon corrosion, may occur. These processes are often associated with a change in the functional groups on the surface of the electrodes, which may lead to a performance loss on the one hand, but also to an additional increase in the degradation rate, as the side reactions are also influenced by the chemical (surface) composition.<sup>[20]</sup> As mentioned above, altered surface structures and functional groups can also benefit the performance of VRFBs, which causes additional challenges in research on degradation. Besides that, the intercalation of various ions, which are present in the electrolyte solution, plays a key role in degradation studies of graphitic structures. The type of the intercalated species as well as conditions such as the pH value or the applied potential have an influence on the reversibility of the intercalation process and the associated mechanical stress.<sup>[21]</sup>

In summary, there are many processes that may influence the stability of carbon-based electrodes and thus the performance of VRFBs, with Figure 1 providing a schematic overview of the mentioned factors. In addition to these direct effects on the carbon material, indirect effects such as enhanced OER and HER activity have also to be considered. Based on these general aspects, the impact on three different carbon-based materials is discussed in the following according to recent studies.

## 2.1. Carbon Paper Electrodes

Carbon paper (CP) is a carbon-fibre-based and porous material in which the individual fibres are non-woven but are held together by a binder.<sup>[22]</sup> NOURANI et al. investigated the degradation of such electrodes in 5 M  $\text{H}_2\text{SO}_4$  solution at 80 °C and a potential of +2.0 V vs.  $\text{Hg}|\text{Hg}_2\text{SO}_4$  over two hours.<sup>[20]</sup> The parameters of this accelerated corrosion protocol were selected to be equivalent to a utilisation period of 615 hours at +1.4 V vs. SHE, which is intended to simulate the long-term conditions at the positive electrode of VRFBs. X-ray computed tomography and electron microscopic examinations showed an increase in the mean pore radii and a delamination of the inner parts of the CP, which the authors attributed to a decomposition of the binder. As a result, a reduced mechanical stability of the material was observed. The degraded electrode was then compared with an as-received sample in full-cell experiments, whereby only the impact on the positive half-cell was investigated. In contrast to the general expectations, the stress test led to an increase of the charge and discharge capacity because of a possible enhancement in electrochemical activity. The authors offered an explanation based on X-ray photoelectron spectroscopy (XPS), amongst other techniques, which showed a significant increase in the carbon-oxygen species on the electrode surface, with 60% of the carbon being in an oxidised state after two hours. The improved activity and wettability of the “degraded” electrode were attributed to the presence of these functional groups. This observation is consistent with the previously noted fact that not all reaction-related changes must have a negative influence on the performance of a carbon-based electrode. However, it is important to mention, that the accelerated corrosion protocol proposed by the authors, although probably quite interesting from a fundamental point of view, is not necessarily equivalent to operation under practical conditions. In particular, the high potentials and concomitant likely very strong OER or the absence of the relevant vanadium ions may lead to specific changes, which are different from those occurring in real VRFBs. These considerations also point to the challenge of finding realistic degradation protocols.

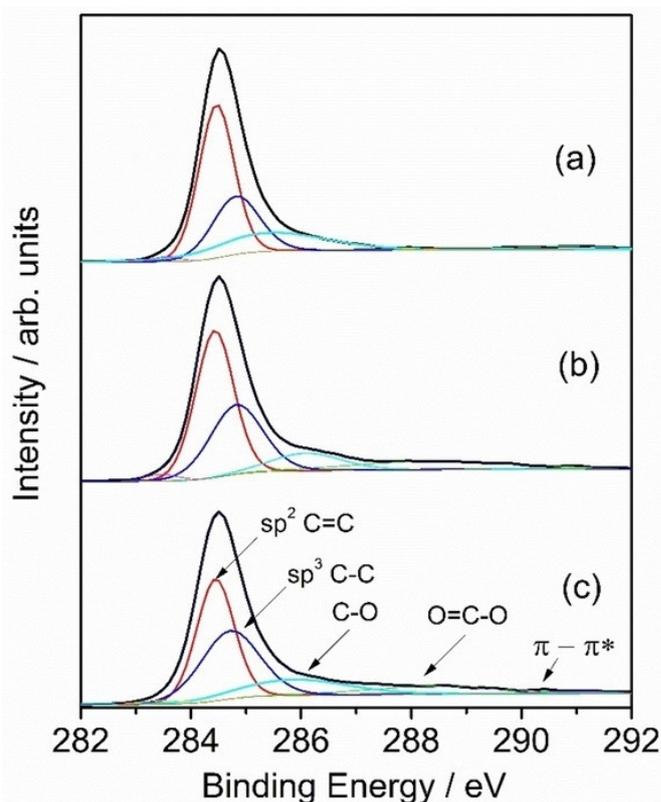


**Figure 1.** Schematic representation of a graphitic structure (black) and possible mechanisms of structural changes by the various influences (red), as mentioned in the text.

Generally, degradation under practical conditions of a full-cell setup, especially in a vanadium-containing electrolyte solution, leads to a reduction in performance, as shown by SINGH et al.,<sup>[23]</sup> for example. The authors carried out 100 charge and discharge cycles at a current density of 80 mA/cm<sup>2</sup> and analysed the structural and electrochemical effects on the electrodes of the positive and negative half-cell. The stress test showed a 70% reduction in charge-discharge capacity, with the causes being suspected to be the degradation of individual cell components, particularly electrodes and electrolyte solution. This result is contrary to the previously described data of NOURANI et al.,<sup>[20]</sup> but in accordance with the studies<sup>[24]</sup> and<sup>[25]</sup>, for example. Following the charge and discharge cycles, SINGH and co-workers used cyclic voltammetry (CV) to analyse the changes of the degraded electrode compared to the as-received material in vanadium-free and vanadium-containing electrolyte solutions.<sup>[23]</sup> In addition to an increase in the specific surface area, they describe an improvement of the OER and HER activity, whereby the degraded positive electrode is more affected by this. In contrast, the negative electrode exhibits higher peak separation of the V<sup>2+</sup>/V<sup>3+</sup> redox couple, which indicates increased irreversibility of the reaction and thus suggests that the negative electrode is more strongly influenced by degradation phenomena directly influencing the relevant redox reactions during full-cell measurements. This general statement is also supported by other studies, independently of the chosen carbon material.<sup>[25,26,27]</sup>

Along with changes of the electrochemical properties, structural alterations, in particular on the electrode surface, were also investigated in the study of SINGH and co-workers.<sup>[23]</sup> XPS analyses (Figure 2) showed that the O/C ratio of the two degraded electrodes (0.22 for the positive and 0.25 for the negative side) increased approximately 10-fold compared to the original material (0.02). On the positive side, this is due to the oxidative conditions, i.e. the highly positive potential and the acidic and oxidising (VO<sub>2</sub><sup>+</sup>) environment. Nonetheless, because of the low electrode potentials and the reducing conditions (V<sup>2+</sup>) on the negative side, the reasons for this must lie elsewhere. The authors propose an explanation based on the oxidative properties of the acidic medium, i.e. the H<sub>2</sub>SO<sub>4</sub> solution. From these considerations it immediately becomes clear that a thorough analysis of formation or reduction of oxygen functional groups during (or at least after) electrochemical processes is of fundamental importance for our understanding of changes in electrochemical properties.

In the as-received case, the electrode material contained almost exclusively hydroxyl groups (–OH), whereas the degraded electrodes showed a mixture of hydroxyl and carboxyl groups (–O–C=O) after long-term treatment. This change is discussed as a possible reason for the progressive performance loss, since hydroxyl groups are considered to be important for the mechanism of the V<sup>2+</sup>/V<sup>3+</sup> and VO<sup>2+</sup>/VO<sub>2</sub><sup>+</sup> reaction.<sup>[14,15,28]</sup> In the negative half-cell, the changes in surface groups also affected the adsorption of the V<sup>2+</sup> and V<sup>3+</sup> ions, which the authors postulated based on voltammetry scan rate analysis. Therefore, despite the general increase in oxygen-containing surface groups, there is a deterioration in the overall perform-



**Figure 2.** Example of changes in the surface composition of carbon-based electrodes during electrochemical stress. Original figure caption: Deconvoluted C1s XPS spectra: a) fresh heat-treated carbon paper; b) positive electrode after 100 VRFB cycles; c) negative electrode after 100 VRFB cycles. Reprinted from Ref. [23], Copyright 2021, with permission from John Wiley and Sons.

ance, which is contrary to the findings of the previously mentioned study. Detailed investigations, particularly using well-defined materials and under precisely controlled conditions, are thus essential (see Chapter 3).

Moreover, RAMAN spectroscopic investigations confirm further structural effects on the carbon-based electrodes after prolonged charge-discharge cycles. For example, the intensity ratio of the D and G band ( $I_D/I_G$ ) was used to draw conclusions about the number of structural defects, with the positive electrode showing an increase while the negative electrode displayed a decrease compared to the as-received material. The authors proposed the different potentials of the two half-cells as a possible cause for these structural differences. They also analysed the relative change in the 2D band, which correlates with the charge carrier density of the degraded materials. Again, differences between the individual electrodes have been detected, which were explained by the polarity and surface functionalities of the materials.

In addition to the properties mentioned so far, there are also other influences that may determine the degradation behaviour of a carbon-based electrode, as PAHLEVANINEZHAD et al. have shown.<sup>[29]</sup> They investigated the influence of impurities in the electrolyte solution on the performance of VRFBs. Usually, impurities from ions, such as Na<sup>+</sup>, K<sup>+</sup>, Mn<sup>2+</sup>,

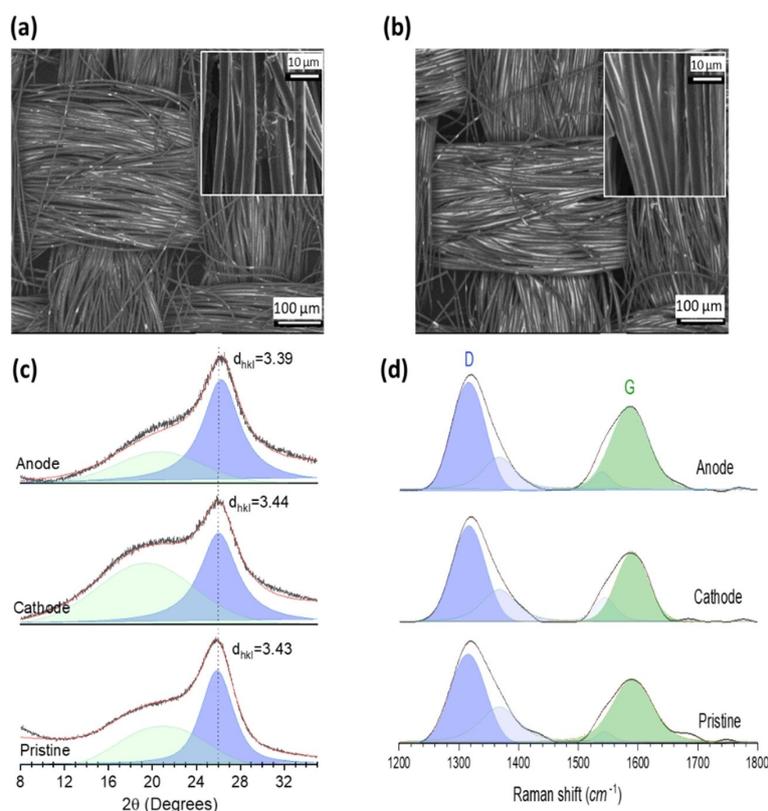
$\text{Fe}^{2+}/\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Al}^{3+}$ , destabilise the dissolved vanadium species and cause the formation of poorly soluble precipitates.<sup>[29,30]</sup> This can affect the overall performance and stability of the system, with deposits affecting processes in the membrane and on the electrodes. PAHLEVANINEZHAD and co-workers examined these effects caused by  $\text{Al}^{3+}$ ,  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  ions, which are commonly present in vanadium-containing ores. Their full-cell measurements showed a reduction in performance over 200 charging and discharging cycles, with a higher impact on the negative half-cell reaction ( $\text{V}^{2+}/\text{V}^{3+}$ ). The most significant negative effects were attributed to  $\text{Al}^{3+}$  ions, followed by  $\text{Fe}^{2+}$  ions, whereas the influence of  $\text{Mn}^{2+}$  ions has been described as negligible. For  $\text{Al}^{3+}$  ions, the performance loss is due to precipitates formed on the electrodes, as shown by SEM-EDS, X-ray diffraction (XRD) and RAMAN spectroscopy. Besides Al, these precipitates also contained V, indicating a destabilisation of the active species in the electrolyte solution. In the presence of all three impurities, the poorest performance was achieved, even though less precipitate was formed. The competing adsorption of  $\text{Al}^{3+}$  and  $\text{Fe}^{2+}$  ions with the relevant V ions is considered to be one of the possible reasons.

## 2.2. Carbon Felt Electrodes

As it fulfils the requirements for an ideal electrode material (see Chapter 1), carbon felt (CF) is widely used in VRFBs.<sup>[18]</sup> Generally,

CF can be produced from two different precursors, namely polyacrylonitrile (PAN) and rayon, with a process temperature of 1200–1600 °C.<sup>[31]</sup> SIVAKUMAR et al.<sup>[13]</sup> studied the long-term degradation of CF electrodes in VRFBs with a focus on the three main factors microstructure, molecular-level defects and surface functionalisation, which determine the properties of the carbon-based material. Using various spectroscopic methods, they concluded about the electrode state after 8000 charge and discharge cycles at different current densities. By means of *ex situ* SEM-EDS, precipitation of individual electrolyte components (mainly based on V and S) was confirmed, although it remains unclear whether these species can be dissolved again under normal operation conditions. Broadened lines in the XRD (Figure 3) indicated the presence of defects within the electrodes, which were attributed to the insertion of certain ions, such as  $\text{SO}_4^{2-}$  ions, or the adsorption of adatoms.

Analysing the spectral intensity ratio of the D and G bands from RAMAN spectra (Figure 3) also revealed an increase in (surface) defects, which may result from heteroatoms or the formation of edge sites. Additionally, the authors examined the overall change in the electrode surface composition using XPS and IR spectroscopy. Both, the negative and the positive electrode, exhibit an increasing content of C–OR and C=O functional groups, whereby the changes correlate with the stability of the electrodes as well as the kinetics of the redox reactions taking place. In conclusion, possible precipitates in the electrode pores, reduced wettability and reaction kinetics



**Figure 3.** Example of structural changes of carbon-based electrodes during electrochemical stress. Original figure caption: SEM image of ELAT carbon cloth electrode taken from the cathode (a) and anode (b) of a VRFB after 8000 cycles. XRD pattern (c) and Raman spectra (d) of pristine, cathode, and anode electrode samples. [...] Reprinted from Ref. [13], Copyright 2021, with permission from American Chemical Society.

due to altered surface groups as well as changed electrical conductivities caused by point defects are discussed as the main reasons for the long-term degradation of the used electrodes and the associated loss in performance.

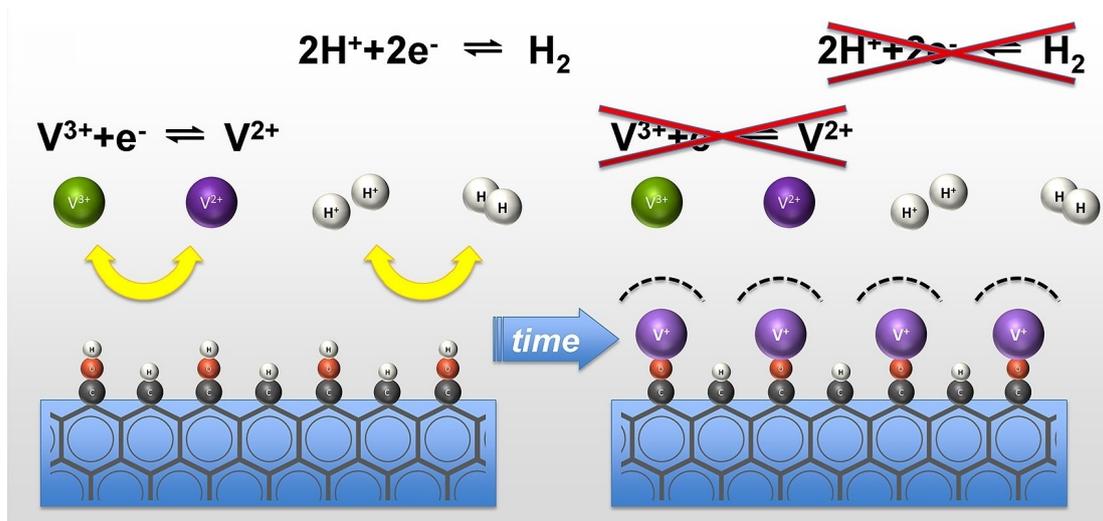
In agreement with the previous observations, SCHNEIDER et al.<sup>[32]</sup> were also able to demonstrate the larger contribution of the negative electrode on the degradation of VRFBs. They used electrochemical impedance spectroscopy (EIS) and analysed the obtained data using distribution of relaxation times (DRT). In an accelerated stress test over two days, the authors found that the positive half-cell is mass transport controlled, while the negative half-cell is limited by the kinetics of the  $V^{2+}/V^{3+}$  redox reaction. The latter thus represents a major part of the overall performance limitation in a full-cell setup. In a further study, SCHNEIDER et al.<sup>[33]</sup> investigated the influence of degradation on bismuth-modified CF electrodes. Bismuth, as well as other elements, is regarded as a promising electrocatalyst for the negative half-cell reaction of VRFBs,<sup>[34]</sup> due to its good electrocatalytic activity and the high overpotential for the parasitic HER.<sup>[33]</sup> Using CV, the authors were able to confirm this assumption based on a smaller peak separation and increased peak currents. Compared to the as-received materials, constantly higher capacities were achieved within 50 charging and discharging cycles at a current density of 100 mA/cm<sup>2</sup>. However, it was found that the modification did not provide any protection against degradation of the negative electrode material. By means of X-ray fluorescence (XRF) spectroscopy, bismuth was detected in the electrolyte solution, which indicates that the catalyst dissolves during cell operation. Subsequent electrochemical half-cell tests demonstrated a strong deactivation of the electrode, so that not even the original values of the as-received CF were achieved. Bismuth therefore must have a significant influence on the degradation rate/mechanism of the carbon fibres.

### 2.3. Graphite Felt Electrodes

The third common electrode material used in VRFBs is graphite felt (GF), which is manufactured from the same starting materials as CF, but carbonised at higher treatment temperatures of 2000–2600 °C.<sup>[31]</sup> Due to its chemical and electrochemical stability, conductivity and mechanical properties, it is considered to be an optimal candidate, although activation of the surface is still essential.<sup>[35]</sup> As already described before, oxygen-containing groups on the electrode surface have a particularly significant effect on the negative half-cell reaction, also with regard to the long-term behaviour.<sup>[26,36]</sup> MAZUR et al. investigated this effect over a period of 2000 charge and discharge cycles on thermally treated rayon- and PAN-based GF.<sup>[35]</sup> The full-cell measurements showed a loss of capacity, which in total is more pronounced for the PAN-based felt. Using nitrogen adsorption and by determining the electrochemically active surface area, the authors showed that this difference in degradation behaviour cannot be attributed to a decrease in the surface area. The investigation of the oxygen-containing surface groups by means of XPS does not provide a sufficient

explanation either, as both, the rayon- and the PAN-based felt, show a similar increase. As a major structural difference, the authors were able to demonstrate that the PAN-based GF showed a significant reduction in  $sp^2$ -hybridised carbon and an associated increase in  $sp^3$ -hybridised carbon. They concluded that, in addition to the specific functional groups on the electrode surface, this may be an important indicator for the degradation behaviour of carbon-based materials in VRFBs.

In a further study, GREESE et al. investigated the impact of thermal and plasma treatment of GF on its (long-term) performance in VRFBs.<sup>[37]</sup> They found that a longer temperature treatment at 400 °C under air atmosphere results in a lower initial charge-transfer resistance ( $R_{CT}$ ) and that its increase during prolonged stress is also lower. Scanning electron microscopy (SEM) and krypton adsorption were used to identify material and surface changes as a function of the thermal treatment time, whereby a roughening and an increased total surface area were observed. While the pure plasma treatment led to a significant increase in oxygen functionalities, the additional temperature treatment reduced their numbers again, as XPS showed. Consequently, the authors concluded that the decrease in the initial  $R_{CT}$ , which corresponds directly to the activity, does not necessarily correlate with the oxygen-containing groups and thus confirm the previous findings by MAZUR and co-workers.<sup>[35]</sup> Instead, an increase in the number of carbon edge-plane surface sites was found, which they associated with the improved properties of the thermally treated materials. For a selected sample, a stress test showed that the  $R_{CT}$  increased by 300% over 400 h of operation, with the degradation rate decreasing over time, assuming that a constant  $R_{CT}$  would result if the test duration is extended. This behaviour was explained based on phenomena observed in the negative half-cell, which GREESE et al. discovered in another study.<sup>[38]</sup> Based on electrochemical investigations on model electrodes, e.g. highly-oriented pyrolytic graphite (HOPG), they postulated a mechanism in which the energetically favoured adsorption of  $V^{2+}$  ions was identified as a cause of the performance loss during (long-term) operation. Thus, at low potentials, the active sites of the carbon-based material are blocked and the  $V^{2+}/V^{3+}$  redox reaction is suppressed. This process is shown schematically in Figure 4, whereby the authors were also able to determine an inhibition of the parasitic HER through the adsorption phenomenon. As the reaction time proceeds, the adsorption rate will decrease when an equilibrium coverage is reached. This observation correlates directly with the declining degradation rate over operation time, which was described above. The authors also demonstrated that reversing the electrode polarity can force the desorption of the  $V^{2+}$  ions so that the original activity can be restored. This does not necessarily require a vanadium-free solution, e.g.  $H_2SO_4$ , but is also possible in a  $VO^{2+}/VO_2^+$  electrolyte solution. Regeneration strategies during the ongoing use of VRFBs are therefore necessary to ensure long-lasting and high-performance operation. However, further investigation strategies, such as different *in situ* spectroscopic methods, are considered necessary to be able to draw final conclusions about the exact processes on the surface of the negative electrode.



**Figure 4.** Postulated surface inhibition of a carbon-based electrode in the negative half-cell of VRFBs by GREESE and co-workers.<sup>[38]</sup> The black dots represent carbon atoms, whereas hydrogen atoms are shown in white and oxygen atoms in red. The hydrogen and oxygen atoms visualise exemplary surface functionalities, which interact with  $V^{2+}$  (green) and  $V^{3+}$  (violet) ions. Reprinted from Ref. [38], Copyright 2021, with permission from Elsevier.

### 3. Systematic Investigations of Degradation Phenomena – A Perspective

The previous chapters clearly demonstrate that there are many causes for the degradation of carbon-based electrode materials. The main influences on degradation behaviour are seen in specific surface functional groups, structural differences (e.g., number of defects,  $sp^2/sp^3$  ratio, share of edge planes, intercalation), as well as the presence of impurities and the formation of adsorbates and precipitates. Furthermore, different experimental approaches were presented to study degradation on the three common systems, i.e. CP, CF and GF. However, it also became evident, that there are no easy and straightforward correlations. For example, long-term degradation may lead to the formation of oxygen functional groups on the one hand but may also influence the share of edge planes in the sample, and both are shown to influence kinetics of the relevant redox reactions. Furthermore different starting materials with their individual structural and surface-chemical features implemented during materials synthesis and pre-treatment impede doubtless attribution of observed electrochemical behaviour to materials-specific causes, and effects of chemical and electrochemical degradation are barely separated. It is thus no surprise that sometimes controversial results are obtained.

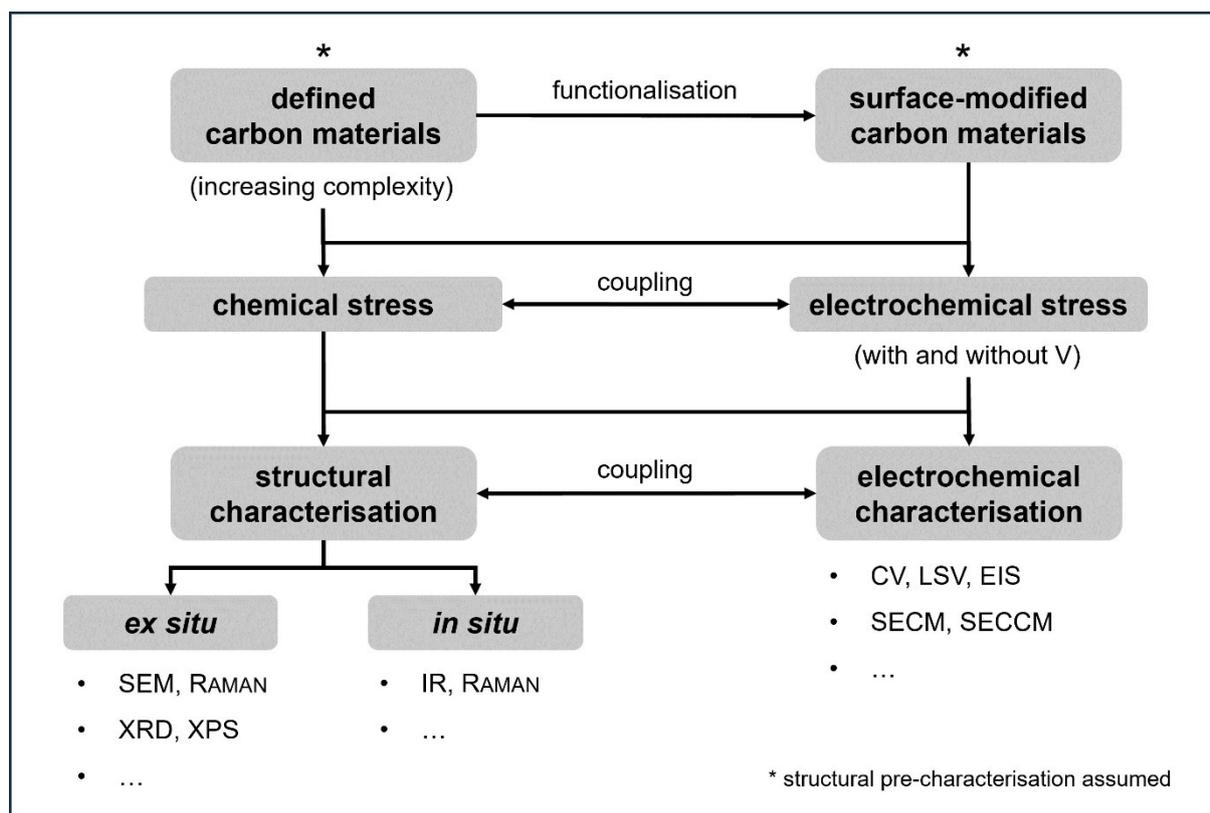
From the authors perspective a systematic investigation of the isolated influences is essential in order to be able to provide reliable suggestions for the development of stable materials. The following section in combination with Figure 5 presents different approaches that, in the authors' view, can deliver a decisive contribution to fundamental research on carbon-based electrodes.

#### 3.1. Reduction of Materials-Related Complexity

The complexity of commercially available electrode materials, for example CP, CF, GF and CC, should be considered as one major limiting factor in systematic investigations, since the broad variety of structural features and also the presence of additives, like binders, may lead to ambiguous or unclassifiable phenomena, even if a thorough characterisation of the materials has been carried out. Here, the use of well-defined model systems, like HOPG or graphene, is recommended, as they allow for a clear proposition of structure-property relationships. For structural and electrochemical characterisation before and after long-term stress, characterisation methods such as RAMAN spectroscopy, XPS, XRD, SEM-EDS, CV and EIS are indispensable.<sup>[39]</sup> The obtained findings can help to understand the degradation behaviour of gradually more complex materials, such as carbon nanotubes (CNTs) or carbon black, in order to finally gain an in-depth understanding of practical electrode materials. The influence of already mentioned factors on structure, such as intercalation processes, changes in the hybridisation of carbon atoms or the presence of impurities, may be much more clearly addressed in this way.

#### 3.2. Investigation of (Oxygen-Containing) Surface Groups

Closely related to the above-mentioned point, the precise investigation of existing surface groups and their influence on the reaction and degradation behaviour has to be addressed. This mini-review has shown that oxygen-containing surface groups on carbon-based electrodes for VRFBs are an impressive example of the fact that not every structural (surface) change necessarily causes a reduction in performance. In this regard, an intense study of the influence of *individual* functional groups, e.g. hydroxyl or carboxyl groups, is of great importance.



**Figure 5.** Schematic representation of the systematic approach, proposed by the authors, for the targeted investigation of degradation phenomena in carbon-based materials. The given characterisation methods can be extended as required.

Functionalisation techniques to selectively form selected functional groups at the surface of carbon materials would be highly desired. However, the variety of possible surface compositions and reaction-related changes complicate this approach, which is why spatially resolved *in situ* techniques (see Chapter 3.4) are an important research tool to address this question.

### 3.3. Separation of Reaction-Related Factors

As argued at the beginning of Chapter 2, various reaction-related influencing factors must be taken into account when analysing the degradation of carbon-based electrode materials. Chemical and electrochemical effects have to be considered, and their impacts should be addressed separately from each other in order to gain a better understanding of their exact effects. Chemical degradation caused by the redox-active vanadium species (see equations 1 and 2) as well as other components of the electrolyte solutions, e.g.  $\text{H}_2\text{SO}_4$  but also impurities, must be considered. The respective impacts have to be analysed with and without application of a potential or a current, to unravel the additional effects of electrochemical degradation. Similar to the previous discussion of the material-related complexity, the use of model electrolyte solutions of increasing complexity, i.e. composition and concentration, is recommended. Furthermore, the investigation of thermal and mechanical degradation cannot be neglected, especially under

operating conditions of VRFBs. Nevertheless, factors such as temperature, flow velocity or compression of the electrodes on the degradation rate, for example, are generally omitted in many laboratory studies, although they are of great importance for comprehensive stability recommendations.

### 3.4. Application of Time- and Spatially Resolved *in situ* Techniques

To gain a further understanding of the described influencing factors, *in situ*-methods provide a fundamental basis. In this way, depending on the method, time and spatially resolved analyses are possible that allow for clear structure-property relationships. *In situ*-RAMAN microscopy with its good spatial and time resolution is able to clarify the fundamental changes in the carbon structure during long-term treatment. The influence of and changes in  $\text{sp}^2$ - or  $\text{sp}^3$ -hybridised carbon atoms or intercalation of ions into the graphite lattice may thus be addressed. Furthermore, blocking of active sites by precipitated vanadium species (see Chapter 2) can be unravelled. *In situ*-IR spectroscopy offers the possibility of characterising surface groups and adsorbates and may support results from RAMAN microscopy on precipitated vanadium species but also monitor changes in surface functional groups. *In situ*-X-ray diffraction on the other hand may support RAMAN spectroscopy with regard to structural changes and in particular intercalation processes.

In combination with microelectrochemical methods, for example scanning electrochemical microscopy (SECM)<sup>[16,40]</sup> or scanning electrochemical cell microscopy (SECCM), detailed correlations between local electrochemical and structural data are possible.

Once again, Figure 5 summarises the proposals for the systematic investigation of carbon-based electrodes. Based on the thus-generated knowledge, materials and reaction-related complexity should be extended as required to close the bridge towards practical electrodes. Factors such as porosity, electrolyte flow rate, electrode compression and presence of other surface functionalities apart from oxygen-containing groups will then have to be addressed. Considering that the overall behaviour of an electrode is a combination of many different influences, it becomes evident how important an exact understanding of the material properties is for the development of reliable systems. Even though interesting model-based concepts for the investigation of VFRBs are already pursued by some groups, for example in the studies<sup>[38]</sup> and<sup>[41]</sup>, they are not used in the suggested systematic and methodological depth. However, this is necessary in order to clarify the sometimes contradictory results of the literature. This also includes the creation of standardised and application-oriented measurement and degradation protocols, which significantly simplify the comparability and transferability of different data sets.

#### 4. Conclusion

This mini-review article summarised the current knowledge gained in the last few years on the degradation of carbon-based electrodes in VFRBs. The focus was set on the most common materials, i.e. CP, CF and GF. In general, it was shown that long-term use of the electrodes is associated with a loss of performance, with the negative half-cell having a greater contribution. However, the reasons for performance loss are less clear and are partly seen in the altered surface functionalities, especially the oxygen-containing groups. But there are also studies that attribute the degradation behaviour to changes in the carbon hybridisation or other surface effects. The adsorption of  $V^{2+}$  ions and their inhibition of the active sites for the  $V^{2+}/V^{3+}$  redox reaction was mentioned as an example. However, the sometimes contradictory results clearly indicate that further studies and approaches are needed to describe the occurring processes more precisely. Only with an accurate understanding of all degradation phenomena it will be possible to develop new types of materials with stable performance over a long service life. Regeneration approaches can also only be developed with respect to these findings. Nonetheless, the structural heterogeneity of carbon-based electrodes as well as the different reaction-related contributing factors make it difficult to determine the individual contributions to the overall degradation rate, so that model conditions and *in situ* studies should be considered in a focussed manner, as shown in the perspective. These results could be gradually transferred to more complex systems. This would help to develop durable carbon-based electrodes and thus improve the long-term

stability of VFRBs as well as promote their application as widespread ESSs.

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#### Conflict of Interests

The authors declare no conflict of interest.

#### Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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