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Microwave-assisted preparation of carbon nanofiber-functionalized graphite felts as electrodes for polymer-based redox-flow batteries

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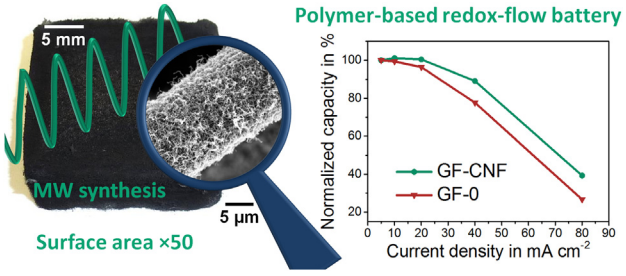
HIGHLIGHTS

- Carbon nanofibers were grown on graphite felt by a microwave synthesis process.
- This increased the active surface area of the graphite felt by a factor of 50.
- The functionalized felts were applied as electrodes for a polymer redox-flow battery.
- An improved current rating of about 45% at 80 mA cm^{-2} was observed.

GRAPHICAL ABSTRACT



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ABSTRACT

A simple and fast microwave-assisted protocol to functionalize commercially available graphite felts (GFs) with carbon nanofibers (CNFs) for the application as electrode materials in redox-flow batteries (RFB) is demonstrated. As catalyst for the CNF synthesis nickel acetate is applied and ethanol serves as the carbon source. By the *in-situ* growth of CNFs, the active surface of the electrodes is increased by a factor of 50, which is determined by the electrochemical double layer capacities of the obtained materials. Furthermore, the morphology of the CNF-coating is investigated by scanning electron microscopy. Subsequently, the functionalized electrodes are applied in a polymer-based redox-flow battery (pRFB) using a TEMPO- and a viologen polymer as active materials. Due to the increased surface area as compared to an untreated graphite felt electrode, the current rating is improved by about 45% at 80 mA cm^{-2} and, furthermore, a decrease in overpotentials is observed. Thus, using this microwave-assisted synthesis approach, CNF-functionalized composite electrodes are prepared with a very simple protocol suitable for real life applications and an improvement of the overall performance of the polymer-based redox-flow battery is demonstrated.

1. Introduction

To enable the further transformation from fossil fuels to renewable energy sources, scalable, low-cost devices for energy storage are urgently required [1]. In this context, redox-flow batteries (RFB) are currently considered as a highly promising

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alternative for the storage of large amounts of energy [2–5]. RFBs consist of redox active materials, which are dissolved in an electrolyte solution being stored in large tanks, a cell stack for conversion and pumps that circulate the electrolyte solution in between these two main components. Their advantage is a straight forward approach towards scalability, since by adapting tank and stack size, RFBs can be tailored for domestic as well as for industrial applications. A large number of redox couples have been studied during the last years, with vanadium based RFBs being the most widely investigated battery system [6,7]. With the advent of organic redox-active materials [8], e.g., quinones [9,10], nitroxide radicals [11–13] or polymers [14–16], questions concerning the right choice of electrode materials, which have already been answered for vanadium RFBs, arise anew. The electrodes employed in the cell stack play a key role for the efficiency of a redox-flow battery system. Ideally, the electrode material should provide a porous structure with large surface area, good electric conductivity, fast reaction kinetics as well as high mechanical stability. Thus, commercially available carbon materials, as for example carbon or graphite felts, carbon paper or graphite powder, are usually applied [17,18].

To improve the electrochemical performance of carbon fiber-based electrode materials, various electrode modification protocols were developed [17]. For vanadium oxide batteries oxygen-containing functional groups are known to facilitate the redox reaction and, furthermore, to improve the wettability of the electrode and, thus, to increase the interaction between the electrode and the electrolyte. The oxygen functionalization of graphite fibers can be achieved by applying different methods [19], for example, by thermal treatment under air atmosphere either by conventional [20] or microwave [21] heating as well as by a treatment with oxygen plasma [20,22] or an electrochemical oxidation in sulfuric acid [23]. Other electrode modifications to achieve an increased activity include the application of catalysts. For example, Mn_3O_4 [24], CeO [25] or bismuth [26] nanoparticles or nitrogen functional groups were introduced [27,28] to facilitate the redox reaction of vanadium ions.

Another approach for an improved electrode performance is to increase the specific surface area (SSA) of the electrode material, in order to increase the number of active sites for the redox process. To enlarge the surface area of a graphite felt (GF), the surface of the microfibers can be functionalized with, e.g., carbon nanofibers (CNFs) or graphene, which increases the SSA by retaining a good electric conductivity. Carbon microfibers can be functionalized by dipping the electrode substrate in a dispersion of carbon nanomaterials, e.g., a CNT dispersion [29] or thermally treated graphene oxide [30]. However, pristine carbon nanomaterials are difficult to disperse and, furthermore, frequently a binder is required [29] to improve the adhesion of the nanomaterials to the carbon microfibers.

The direct growth of carbon nanostructures on the carbon support bears the advantage that no binder is required and, furthermore, no handling or dispersion of nanopowder is required.

Several methods are known to synthesize CNFs, with chemical vapor deposition (CVD) being the most popular one [31]. By applying different variations of the CVD approach, carbon or graphite felt-based electrodes were functionalized with carbon nanofibers [32,33], nitrogen-doped CNTs [34], mixtures of CNFs and CNTs [35] or graphene-nanowalls [36] and the resulting increase in active surface area was observed to improve the performance of vanadium redox flow batteries in all cases. However, the CVD synthesis of CNFs is a rather slow process, which commonly requires several processing steps at a high temperature of more than 600 °C for up to several hours under an inert atmosphere [33–35].

In this respect, microwave heating offers a fast and simple alternative to synthesize CNFs [37]. By microwave irradiation, carbon-based substrates can be heated to several hundred degree Celsius within a short time scale of a few minutes or even of just seconds [38], thus enabling the development of microwave-based CNF synthesis approaches similar to the CVD process, but with a tremendous reduction of the processing times [39,40]. When a substrate, which is coated with a suitable catalyst, is heated in the presence of a hydrocarbon as the carbon source, CNFs can be synthesized within one single microwave irradiation step. During this irradiation step the whole process is taking place, from the reduction/decomposition of the catalyst precursor till the nucleation and growth of the CNFs. Furthermore, no inert conditions are required and the process can be performed at ambient conditions, which makes it additionally facile and fast. Thus, it has become an attractive method to obtain CNF-functionalized surfaces [40].

Herein, we report the direct growth of CNFs on graphite felts using a microwave-based synthesis approach with nickel acetate as catalyst and ethanol as the carbon source. The CNF-functionalized graphite felt (GF-CNF) is investigated by scanning electron microscopy (SEM) and Raman spectroscopy. The relative differences in the specific surface areas between modified and unmodified graphite felts are investigated by the determination of the electrochemical double layer capacity. Finally, the GF-CNF was tested in a polymer-based redox-flow battery (pRFB) using a TEMPO- and a viologen polymer as active materials to evaluate the influence of the increased surface area on the performance of the battery.

2. Experimental

2.1. Preparation of CNF-functionalized electrodes

The synthesis of carbon nanofibers was performed with a similar set-up as previously described [40]. Briefly, the microwave-assisted synthesis approach is based on a catalyst-coated substrate, which is heated by microwave irradiation in the presence of ethanol, which serves as the carbon source. As substrate for the electrodes, a graphite felt of 6 mm thickness (GFA6, SGL Carbon) was cut into pieces of 2.25 cm × 2.25 cm. For the deposition of the catalyst, the GF was immersed in a 10 mM ethanolic nickel acetate solution for 3 h and was afterwards left to dry in air. An acid treatment (3 h in sulfuric acid) and a 3 min Argon Plasma treatment (300 W, Plasma system Nano, Diener Electronic, 3 min from both sides) was carried out prior the catalyst deposition to improve the wettability of the substrate.

The CNF synthesis was performed using a multimode microwave Synthos 3000 (Anton Paar). This microwave handles large vials and, thus, allows the functionalization of electrodes in the required size. A piece of quartz tube was used to place the catalyst-coated GF above the reservoir of the liquid ethanol (3 mL). To initiate the CNF growth the full power (1400 W) of the microwave was applied for five to 10 min. Subsequently, the overpressure resulting from the gaseous by-products of the carbon formation was released [40] and the microwave treatment was repeated two more times to enable further CNF growth.

Caution: During microwave irradiation of graphitic materials high temperatures might (locally) arise [37]. Thus, components with low melting point should be avoided in close vicinity to the graphite felt and the irradiation time should be increased carefully if such experiments are implemented with a new microwave system.

2.2. Characterization

2.2.1. Characterization of the CNF coating

Scanning electron microscopy imaging was performed with a