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Carbon Colloids Prepared by Hydrothermal Carbonization as Efficient Fuel for Indirect Carbon Fuel Cells

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The idea for the electrochemical conversion of the potential energy of coal into electrical energy originates from the late 19th century, when W. Jacques introduced the principle of the noncombustive, electrochemical oxidation of carbonaceous matter by air.[1] Carbon fuel cells are conceptually the most effective way of converting the chemical energy of carbon into electrical energy, especially compared to classical combustion processes. Additionally, since the global reserves of coal exceed by far the reserves of other fossil fuels, in the past decades there have been numerous attempts to develop and improve generally applicable carbon fuel cells,[2−9] promising higher efficiency compared to conventional coal combustion.

Past and current research activities on carbon fuel cells have been strongly focused on the direct electro-oxidation of the carbonaceous fuel. These direct carbon fuel cells (DCFC) require temperatures between 500 and 1000 °C because of the high activation barrier of the electrochemical oxidation of coal.[10,11] Different approaches have been investigated to realize DCFCs: W. Jacques used a molten hydroxide as electrolyte. In this case the undesirable side reaction of the developing CO_2 with the hydroxide leads to the formation of carbonates and thus a consumption of the electrolyte. Nonetheless, this concept had been readopted later.[6] More recent studies describe the use of other electrolytes for DCFC, such as molten carbonates (MCFC). For example, Li_2CO_3/K_2CO_3 mixtures are suitable electrolytes because of their high conductivity, their stability in the presence of carbon dioxide, and their suitable eutectic melting temperature. Various approaches have been made performing the electro-oxidation in coal−electrolyte slurries.[3−5,7,8] In other attempts solid-oxide electrolytes have been applied for DCFC systems.[2] Very recent works even presented hybrid systems, combining the molten carbonate and solid oxide electrolyte.[9]

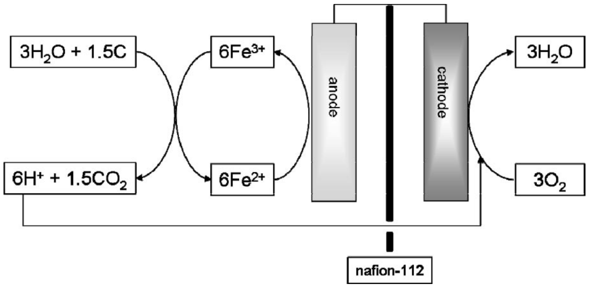

Figure 1. Schematic representation of the secondary redox concept for an indirect carbon fuel cell.

However, as these high-temperature setups are limited to stationary applications, also alternative concepts for carbon fuel cells were investigated. Thus, a secondary redox system for the oxidation of coal was introduced: Here the carbon is not directly oxidized at the anode but by a suitable oxidant, which is renewed, that is reoxidized, at the anode. A schematic representation of the concept for an indirect carbon fuel cell is shown in Figure 1. The great advantage of this approach is the considerably lowered activation barrier compared to the direct electrochemical oxidation of carbonaceous materials. This enables the operation of such a cell at about 80−100 °C, thus widely expanding the spectrum of potential applications. However, a loss of effectivity caused by the secondary redox system mediating the oxidation of the carbon source is to be stated. The decrease of cell voltage theoretically lies in the range of 50%, as we expect a reduction from 1.02 V[12] to 0.51 V.

Numerous studies have been carried out on the subject of this type of oxidation of coal mostly focused on the search for a suitable secondary redox system. In this respect mainly transition metal redox couples were identified as suitable for this type of fuel cell.[10,13−15] A first setup modeling an indirect carbon fuel cell in which the oxidation of coal was mediated by a secondary redox system was however just recently presented by Whitesides et al., applying Fe^{3+}/Fe^{2+} as a secondary redox system in the anodic half-cell. Using a subbituminous fossil coal as fuel, promising results were achieved; however, more favorable oxidation properties and thus a new potential carbon source consisting of small, dispersible particles were requested.[11]

This contribution intends to increase the efficiency of indirect carbon fuel cells using carbon colloids as a fuel, prepared by a process called hydrothermal carbonization

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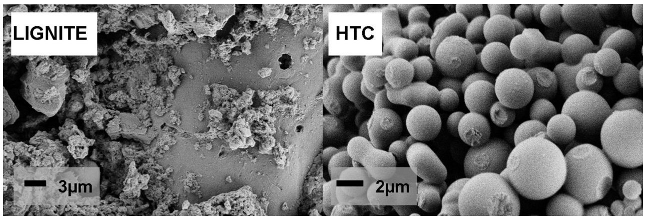

Figure 2. SEM images of lignite and HTC coal. The micrometer-sized spherules of HTC coal dispersions are clearly visualized.

(HTC):[16−20] Heating carbohydrates in water in a closed reaction vessel for 4−24 h to temperatures of around 200 °C yields such water dispersible carbon colloids. HTC has a number of other practical advantages: Once activated, HTC is a spontaneous, exothermic process, liberating up to a third of the combustion energy stored in the carbohydrate throughout dehydration. In addition, most of the original carbon stays bound to the final structure. Carbon structures produced by this route are therefore the most CO_2-efficient.[18] The idea of HTC dates back to the beginning of the 20th century, when first hydrothermal conversions of carbohydrates into coal-like materials were observed by investigating the natural formation process of coal,[21−23] and there was a recent renaissance of this method[16,17] initiated by numerous works on the subject, from applying HTC for material science up to the use of crude plant material as carbohydrate source.[18−20,24,25] Thus a more sustainable and environmentally friendly approach can be envisaged when hydrothermally treated biomass is used as carbon source for an indirect carbon fuel cell, yielding in an overall zero-emission balance concerning greenhouse gases.

A hydrothermally carbonized carbohydrate (D-glucose) is applied as a carbon source for the use in an anodic half-cell. In this respect the glucose can be regarded as a model compound for several biomass sources, which have been shown to yield comparable carbon morphologies upon hydrothermal carbonization.[20] Besides the expected zero balance of carbon dioxide, there are further advantages combined with the use of hydrothermally carbonized coal: The open and hydrophilic surface structure which can be proved by the bands of hydroxylic and carbonylic groups in the FTIR spectrum (see Figure S1, Supporting Information) of HTC coal is expected to raise its oxidizability. Additionally, the micrometer sized spherical particles (Figure 2) and the amorphous character of the structure should be ideal for a water-based fueling system. Furthermore, the inherently low contents of sulfur and ash avoid disturbing interactions with the secondary redox systems. For glucose as the model component for biomass in HTC, these impurities are practically zero, which makes it an ideal model system for this study.

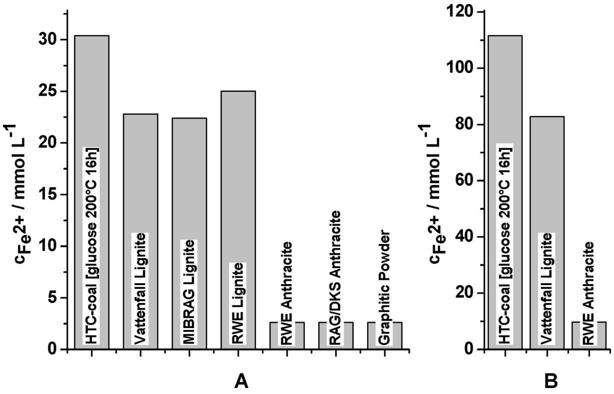

Figure 3. Different coal types and their oxidation by the secondary redox system. Tested by heating 100 mg of the coal sample in a 0.5 mol L^{-1} solution of $FeCl_3$ in sulfuric acid to 100 °C. Amount of formed Fe^{2+} was determined by dichromatometric titration. A: 30 min. B: 16 h.

To evaluate the potential of HTC coal as a fuel, the oxidation properties of this carbon source compared to fossil coals is of main importance. Different samples of lignite and anthracite were applied as reference materials, using a simple Fe^{3+}-oxidation assay. The experiments revealed a significantly better capability of hydrothermal coal derived from glucose to get oxidized: it highly exceeds anthracite in its oxidation rate but also shows better oxidation properties than lignite (Figure 3). The reason of the lower oxidation rates of anthracite and pure graphitic carbon can probably be found in their dense, ordered structure of stable aromatic graphene sheets, which can only be slowly oxidized by Fe^{3+}. For lignite the structure is more open and amorphous, thus making the carbon better accessible for oxidation. Beside the high amount of surface funcionalities (Figure S1, Supporting Information), which are very likely important for at least the initiation of the oxidation process, HTC coal features a chemical structure mainly composed of aliphatic and olefinic building units, which are highly reductive and reactive, while the amount of conjugated aromatic rings is markedly low.[26] The micrometer-sized spherical particles additionally offer a more accessible surface for the heterogeneous oxidation process. As a result of its hydrophilic surface the carbon can further be easily dispersed in $FeCl_3$/water solutions without any processing aids, which add some secondary benefits to the handling of the fuel.

Therefore we attempted to employ HTC coal in a model anodic half-cell, similar to the one described by Whitesides et al. In this model system, the cathodic oxygen half-cell has been replaced by a VO^{2+}/VO^{2+} half-cell,[11] making the procedure more suitable to be run on the laboratory scale while the redox potential is close to the one of oxygen. Reference measurements were carried out between a half-cell containing only a Fe^{3+} solution and the VO^{2+}/VO^{2+} half-cell. As expected, the measured current was negligible. After replacing the Fe^{3+} solution in the anodic compartment by a mixture of 50 mL of Fe^{3+} solution and 1 g of HTC coal that

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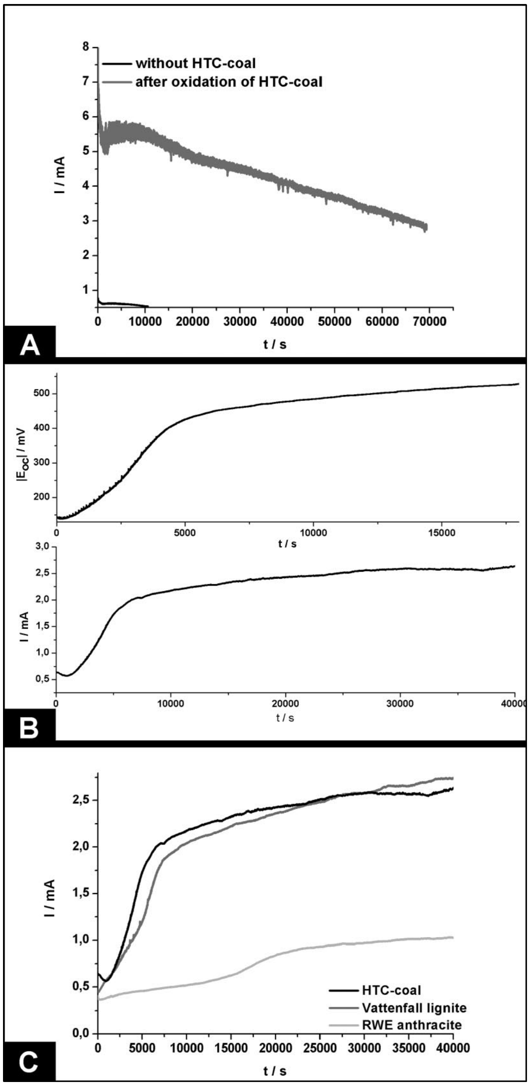

Figure 4. A. Current/time diagram for the oxidation of HTC coal in an indirect carbon fuel cell. Solutions of Fe^{III} and V^{V} were prepared in 0.5 mol L^{-1} H_2SO_4. Separation of half-cells was realized by a Nafion membrane. Carbon felt was used as electrodes. B. Increase of open circuit potential E_{oc} (up) and current I (down) due to Fe^{2+} formation in the anodic half-cell via oxidation of HTC coal. Charge equalization between the two half-cells was assured by a salt bridge containing a saturated KCl solution. Carbon felt was used as electrodes. C. Comparison of hydrothermal and fossil carbon sources.

had been stirred at 100 °C for 3 h, the measured current increased significantly. This can be attributed to the formation of Fe^{2+} ions, which are reoxidized at the anode, thus enabling the flow of current.

Figure 4A displays the course of this electric current with time. A considerable current is observed right from the start of the electrochemical reaction, because a pretreated Fe^{3+}/coal solution was used. If the HTC coal is added to the anodic compartment without pretreatment, the redox equilibrium has to set-in with time. This increase of current is, however, rather fast, and a plateau is reached after approximately 1 h of reaction. In this respect, it can be seen that the formation of Fe^{2+} ions by the oxidation of the carbon source leads to an increase of both open-circuit potential and, in the case of short circuiting both half-cells, electric current (Figure 4B). For comparison, similar experiments were carried out using fossil coals as fuels. The results are in good agreement to the previous experiments on the oxidation ability of different carbon sources. Thus, hydrothermal coal and lignite cause a rather similar increase of the electric current, while this is significantly weaker for anthracite (Figure 4C). The efficiency of this model half-cell can be easily calculated from those curves: 1 g of hydrothermal coal contains about 25 kJ of energy. From the previous oxidation experiments there can be calculated an approximate coal consumption of 4% after 16 h. Current−time integrations reveal, considering as well the potential of the system, efficiencies of ~4% for the salt-bridge-based setup and of ~14% for the membrane-based system, which is, in spite of the academic, nonoptimized setup, already quite satisfying, even though there are surely further steps necessary to promote utilization of this process in real life applications. The difference between the achieved efficiencies of the two setups is most probably caused by the better performance of the Nafion membrane for charge equilibration; nevertheless, the salt-bridge based setup was preferred for the majority of the concept-proving experiments due to its better reliability.

Finally, using carbon colloids derived from hydrothermally treated biomass would indeed yield an indirect carbon fuel cell with an overall zero-emission balance concerning the green house gas CO_2.

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Supporting Information Available: Detailed experimental procedures of the prepartion of the coal samples, the fuel cell setup, and FT-IR spectra of the carbon fuel. This material is available free of charge via the Internet at http://pubs.acs.org.

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