Structural and electrochemical properties of MnO$_2$-Carbon based supercapacitor electrodes

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Abstract

We present results of an approach to incorporate redox-active manganese oxide into the 3-dimensional porous structure of carbon xerogels under self-limiting electroless conditions. By varying the structure of the carbon backbone, we found that deposition of manganese oxide preferably takes place on the external surface area of the carbon xerogels. From our detailed analysis we conclude that 3-dimensional carbon xerogels with particle and pore sizes ranging from 10 to 20 nm and low manganese oxide precursor concentration combined with long deposition times are beneficial for fast operating pseudocapacitance electrodes with high capacitance and effective use of the redox active component.

1. Introduction

In times of rising energy costs energy efficiency is the most urgent task to be addressed. A possible strategy is the reuse of energy e.g. generated upon deceleration of various kinds of movements in industrial manufacturing processes or automotive applications. This is the key application for supercapacitors, storing and releasing electrical energy on the timescale of seconds [1-4]. In order to reach higher energy densities on this timescale, research is extending to faradaic storage processes superimposed to the double layer storage in electrochemical capacitors. Due to the characteristic linear dependence of the faradaic current

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on the applied voltage, this kind of faradaic storage (e.g. in ruthenium dioxide or certain conducting polymers) is called “pseudocapacitance” [1].

In 1999 Lee and Goodenough [5] described a pseudocapacitive behavior of manganese oxides (MnO$_x$) in aqueous electrolytes. Since then, research activities on this relatively easy to handle and abundantly available material continuously increased, due to its obvious advantages over other pseudocapacitive materials. For instance, compared to the also promising ruthenium dioxides, MnO$_x$ does not require strong acidic electrolytes, is less toxic and much cheaper in production.

Since the fast redox-charge storage in MnO$_x$ was identified to take place mainly on the surface of the material, efforts were focusing on optimized structural design of hybrid electrodes [6]. Such approaches range from simply mixing carbon as a conductive agent, MnO$_x$ and a binder [7–9], to thin film deposition [10, 11] and templating [12, 13]. Alternatively, electrolytic deposition of MnO$_2$ into (activated) microporous carbon xerogels, as suggested by several groups, e.g. Cross et al. [10], will employ the micropores at the surface of the primary particles and therefore increases the total amount of MnO$_2$ available for charge storage. A promising approach based on electrodeposition was recently published by Lin et al. [14], making them able of incorporating high amounts of MnO$_2$ into the electrode. By directly contacting the carbon skeleton of the electrodes, they surmount the contact resistance of MnO$_2$ at the current collector-electrode interface and obtained electrodes with very high charging rates.

Fischer et al. [15, 16] chose an approach of electroless deposition of MnO$_2$ on a microporous carbon aerogel (CA) from aqueous solution of NaMnO$_4$ under self-limiting conditions. This was found to be an easily scalable and, in terms of experimental effort, not very demanding method to incorporate MnO$_2$ into the well interconnected porous structure of the CA. Compared to simply mixing CA and MnO$_2$, coating of the CA particles by a thin layer of MnO$_2$ ensures a better electrical contact between the poorly conducting MnO$_2$ and the carbon backbone.

Though they demonstrated in their first study [15] they showed that for neu-
tral solutions, MnO$_2$ penetrates deeply into the aerogel structure, the exact location of the oxide remained unrevealed, leaving it open whether MnO$_2$ resided in the micropores of the carbon backbone or on the enveloping surface area of the carbon xerogel primary particles (“external surface area”). Since the location of the active material in the electrode is crucial for its efficient use in charge storage, we adapted Fischer’s approach on CA reference systems to further investigate the location of the MnO$_2$ deposits.

Due to their variable structural properties, carbon aerogels form an ideal model system to investigate the influence of structural aspects in electrode design on the resulting performance of the electrodes. The three-dimensionally interconnected microporous skeleton of CAs provides huge surface areas advantageously for both double layer charge storage and MnO$_2$ deposition, as well as good electrical conductivity. The well-linked network of interparticular mesopores [17] ensures excellent electrolyte transport. Depending on the size of the primary particles, their envelope surface area, also denoted as external surface area ($S_{\text{ext}}$), can be easily varied. For our study, we used carbon xerogels, which have the same structural properties as the aerogels described above. However, in contrast to aerogels, xerogels are synthesized by drying the organic precursor sub-critically, making the process substantially easier to handle.

Addressing the method of electroless deposition, in a first step we analyze the influence of deposition time and manganese oxide precursor concentration on the deposition of MnO$_x$ on the carbon xerogel backbone and their impact on the resulting electrochemical behavior of the electrodes. Based on this information, we determine a relationship between MnO$_x$ deposition and external surface area of the carbon xerogel by varying the properties of the carbon backbone, i.e. the primary particle size and thereby the external surface area.
2. Experimental

2.1. Preparation of electrodes

Fiber reinforced carbon xerogels (CX) were prepared with different particle sizes yet similar density in order to create a carbon backbone with different external surface area but similar porosity and specific micropore volume. To achieve this goal, we used an accelerated sol-gel route as described in [18]. Carbon paper (Sigratex, SGL group) was soaked with the sol, having a molar ratio of resorcinol to catalyst (0.1 N NaCO$_3$) of 500, 3000 and 8000 and yielding CXs with small, medium and large primary particles, respectively. The mass ratio of resorcinol and formaldehyde to total mass (including water) was chosen to be 28 for all samples. The molar ratio of resorcinol to formaldehyde (37 % aqueous solution) was 1:2. After gelation for 24 hours at 85°C, the residual water was exchanged for ethanol before subcritical drying. The samples were dried in ambient atmosphere at room temperature for three days. Subsequently, the sheets of fiber supported organic xerogel were pyrolyzed under argon atmosphere for 60 min at 850°C, resulting in about 200 µm thick, fiber reinforced carbon xerogel sheets. The mass fraction of the carbon fibers was about 40 %.

To incorporate the manganese oxide active material into the carbon structure, a (self-limiting) deposition process, as described by Fischer et al. [15,16], was employed. Briefly, a carbon xerogel was immersed into an aqueous solution of 0.05 M Na$_2$SO$_4$ and placed under mild vacuum for 30 min to ensure removal of residual gas and thus complete wetting of the xerogel pores. Subsequently, the solution was exchanged for an aqueous mixture of 0.1 M Na$_2$SO$_4$ and 0.1 M NaMnO$_4$. For the variation in precursor concentration, the amounts were adjusted accordingly. The deposition took place over periods of 5 minutes to 24 hours. No evolution of CO$_2$ was observed. We therefore assume a deposition mechanism as described by Ma et al., in which MnO$_2$ is formed on carbon surfaces without releasing carbon during the process [19]. After deposition, the electrodes were rinsed with distilled water until the rinse was optically clear, then immersed in fresh H$_2$O and placed in vacuum for 30 min. This
exchange cycle was repeated three times, ensuring comprehensive removal of residual NaMnO$_4$. After drying for 24 hours at 85 °C, the mass of the hybrid electrodes (CXMn) was determined.

2.2. Structural characterization

Surface morphology of the samples was investigated with a Zeiss Ultra plus scanning electron microscope (SEM). The pore structure of the bare CX and the CXMn samples was analyzed via nitrogen gas sorption at 77 K. The measurements were performed with a Micromeritics ASAP 2020 System. The samples were degassed prior to sorption analysis in vacuum at 300°C for 24 h. The crystalline state of MnO$_2$ is known to change with temperature [20]. This morphological modification seems to leave the microstructure unchanged on length scales probed by gas sorption measurements: No significant changes in the isotherms were observed for hybrid samples degassed at 110°C, compared to isotherms recorded after heating to 300°C.

The total surface area was determined using BET (Brunauer-Emmet-Teller) theory [21]; the external surface area $S_{\text{ext}}$ and micropore volume $V_{\text{mic}}$ were determined by means of the t-plot method [22] [23]. The size of the primary particles $d_{\text{part}}$ of the bare carbon xerogel was estimated from $S_{\text{ext}}$ and the particle density $\rho_{\text{part}}$ assuming spherical particle geometry:

$$d_{\text{part}} = 2 \frac{3}{S_{\text{ext}} \cdot \rho_{\text{part}}}$$  \hspace{1cm} (1)

with

$$\rho_{\text{part}} = \frac{1}{\rho_C + V_{\text{mic}}}$$  \hspace{1cm} (2)

and a carbon bulk-density of $\rho_C = 2.2$ g cm$^{-3}$ [18].

The surface chemistry of representative CX and CXMn samples was investigated via x-ray photoelectron spectroscopy (XPS). The spectra were acquired using a monochromatic Al-Kα excitation at 1486.6 eV and an Omicron EA 125 electron analyzer. The spectra are normalized to the C1s peak and standard Shirley background correction has been carried out.
2.3. Electrochemical characterization

For the electrochemical measurements, a circular electrode ($d = 19$ mm) was cut and weighted. Electrochemical characterization was performed in a home built sandwich cell, made of Teflon with titanium current collectors. The electrode under investigation is separated by a glass paper from a carbon xerogel electrode, which serves as counter electrode. Voltages were measured versus an Ag/AgCl reference electrode. In $1 \text{ M } \text{Na}_2\text{SO}_4$, pure carbon electrodes were cycled within a voltage window from -0.5 to 0.5 V vs. Ag/AgCl, while hybrid electrodes were measured from -0.2 to 0.8 V vs. Ag/AgCl. Prior to each measurement, the electrodes were vacuum infiltrated and cycled several times at 10 mVs$^{-1}$ until the voltammogram of subsequent cycles showed less than 3% deviation from the preceding ones. Afterwards, at every scan rate 3 cycles were measured in total but only the last one was used for analysis, in order to guarantee stable conditions during the measurement. The gravimetric differential capacitance $C$ was calculated from the measured current $I$ and the applied scan rate $dU/dt$, divided by the total mass of the electrode $m_{el}$:

$$C = \frac{I}{dU/dt \ m_{el}}. \quad (3)$$

The total gravimetric capacitance $C_{grav}$ of the electrode is given by the arithmetic mean of the integrated current of the half cycles divided by the measured voltage window. The electrochemical measurements were conducted using an Ivium-n-Stat potentiostat/galvanostat and frequency response analyzer.

3. Results and Discussion

3.1. Fiber reinforced carbon xerogels

Figure 1 shows representative SEM micrographs of the samples used in our study. The first row displays the well interconnected network of the bare carbon xerogels with small (S), medium (M) as well as large (L) particle sizes (left to right). Distinct inter-particular meso- and macropores can be observed.
The N$_2$-gas sorption isotherms are shown in Figure 2. The data are normalized to the mass of the carbon xerogel content of the fiber reinforced material. The isotherms show the typical shape for microporous materials, characterized by a sharp increase in adsorbed volume at relative pressures $p/p_0 < 0.1$, corresponding to micropore filling. In the intermediate relative pressure range, the absorbed volume is larger for samples with small particles than for samples with large particles, indicating an increase in external surface area with decreasing particle size, as expected. For relative pressures above 0.8, a hysteresis loop is observed, which can be related to condensation of N$_2$ in mesopores. The hysteresis loop is more pronounced for small particles and decreases for larger particles, hinting at a shift in inter-particular pore size from meso- to macro-pores and thus to a regime that is not detectable by N$_2$ sorption.

Although BET theory is known to give defective absolute surface area values for microporous carbons, it delivers comparable qualitative results for our samples, assuming the size of micropores being similar for all carbon xerogels under investigation [17, 24, 25]. This assumption can be rationalized by the identical conditions of sample preparation with respect to the precursor system resorcinol-formaldehyde, curing and pyrolysis step. Additionally, we investigated the microporosity of the carbon xerogels in a separate study, by means of CO$_2$-sorption density functional theory-analysis in combination with small angle X-ray scattering, finding similar micropore size distributions for all resorcinol-formaldehyde derived samples, independently of the primary particle size [26].

The results of BET- and t-plot analysis are compiled in Table 1. The errors for $S_{\text{ext}}$ for small particle size samples are mainly influenced by the error of about 10 % in determining the carbon fiber content of the sample. For large particle size samples, the deviation is given by the error of the sorption measurement, with high uncertainties for big interparticular pores. For $S_{\text{BET}}$ and $V_{\text{mic}}$, the uncertainty is mainly influenced by the determination of the fiber content, and therefore amounts to 10 % for all samples. Quantitatively, the external surface area $S_{\text{ext}}$ decreases from 302 m$^2$g$^{-1}$ over 74 m$^2$g$^{-1}$ to 7 m$^2$g$^{-1}$ for the small, medium and large particles, respectively. This trend will be important
for interpretation of the results on MnO$_2$-deposition described later. From the
gas sorption data, primary particle sizes can be calculated (Eqn. [1]) yielding 12,
53 and 462 nm for samples with small, medium and large particles, respectively
[15].

Figure 3(a) shows the cyclic voltammogram of the fiber reinforced carbon
xerogels electrodes. A butterfly-shaped CV curve with a pronounced minimum
at 0.02 V vs. Ag/AgCl, which is well-known for microporous carbons is observed
[27, 28]. With increasing particle size, a sieving effect evolves, indicated by a
decrease in the anodic current [26, 27, 29]. Additionally, a bump, becoming
more pronounced with increasing particle size, arises. This bump is generally
explained by redox reactions of surface groups. However, surface sensitive x-ray
photoelectron spectroscopy (XPS) analysis indicates similar groups with respect
to their valency for all our resorcinol-formaldehyde derived carbon xerogels.
We therefore assume that during charging, SO$_4^{2-}$-ions are forced into pores
until all accessible storage sites are occupied, resulting in a broad peak around
0.15 V vs. Ag/AgCl, at 2 mVs$^{-1}$ (see Figure 8, Supporting Information) [30].
These trapped ions are not completely released at the reversed voltage of same
absolute value as for trapping; rather the ions become released at higher negative
voltages, leading to an increase of negative currents around -0.4 V vs. Ag/AgCl.
Another indication for this trapping process is the disappearance of the bump
upon ion release with increasing scan rate (Figure 8, Supporting Information).

3.2. Fiber reinforced carbon-MnO$_2$ xerogels

3.2.1. Variation of deposition conditions

In a first series of MnO$_2$ hybrid electrodes, we varied the concentration of
NaMnO$_4$ precursor and the deposition time, in order to investigate the impact of
the synthesis parameters on the resulting electrodes. For convenience and being
verified later in this study, from now on manganese oxide refers to MnO$_2$. The
carbon sample used in these experiments was similar to carbon sample S (Table
1), i.e. a fiber reinforced carbon xerogel with a particle size of about 15 nm and
external surface area of about 300 m$^2$g$^{-1}$. In Figure 4(a) the mass of MnO$_2$
per total mass of the electrodes is plotted versus deposition time for various concentrations of the NaMnO$_4$ precursor. At precursor concentrations between 0.01 M to 0.2 M NaMnO$_4$ the deposition times were varied from 5 minutes to 24 hours. For the 0.01 M solution, the mass uptake saturates at high deposition times. This can be attributed to a depletion of MnO$_4^-$ content in the precursor solution, as indicated by the transparency of the solution after about 20 hours. For all samples, a strong increase in mass can be observed at short deposition times. Towards longer deposition times, the slope of the uptake monotonously decreases, but no saturation as expected for a self-limiting process is observed in the applied time range [16].

In Figure 5(a) the CV-curves for samples with an MnO$_2$ mass loading of around 20 wt.% are plotted. Within the range of experimental error, the electrodes show the same electrochemical behavior, thus yielding about the same capacitance value. Samples with a mass loading around 50 wt.% are plotted in Figure 5(b). They also contain similar wt.% of MnO$_2$, but the CV-curve is more disturbed than for samples with a lower MnO$_2$ wt.%. Especially for the 0.08 M electrode, the slope at around -0.2 V vs. Ag/AgCl is less steep, hinting for an increased resistance of the electrode.

Figure 4(b) shows the gravimetric capacitance, calculated from CV measurements at a scan rate of 5 mVs$^{-1}$ for all electrodes shown in Figure 4(a). As one can clearly see, for manganese oxide weight percentages up to about 35 %, the capacitance only depends on the mass of MnO$_2$ that was deposited, rather than on the concentration of NaMnO$_4$ in the precursor or the deposition time. In other words, the microscopic process of MnO$_2$ infiltration into the electrodes is of negligible importance, only the amount of MnO$_2$ matters.

For mass uptakes above 50 wt.% however, the precursor concentration influences the capacitance significantly. Whilst for the 0.05 M sample a continuation of the linear trend can be seen, a pronounced deviation occurs for higher MnO$_2$ concentrations. These results can be interpreted by a higher amount of MnO$_2$ that is not actively participating in charge storage for the samples prepared at precursor concentrations higher than 0.05 M. In this case, the additional MnO$_2$
only adds mass to the electrode. From a structural point of view, this MnO$_2$ might be deposited as thick layers or agglomerates being inaccessible for the electrolyte. For the 0.05 M sample however, due to the lower concentration of MnO$_4^-$-ions, deposition is assumed to take place more slowly, allowing a more homogeneous distribution of MnO$_2$ across the electrode. Further investigations on this microscopic model by small angle x-ray diffraction are forthcoming.

Recently, molecular dynamics simulations have shown that in NaCl aqueous solution ions cannot enter pores smaller than 1.2 nm if no external voltage is applied [31]. Therefore, the assumption proposed by Fischer et al. [16] that sulfate ions enter micropores by vacuum infiltration and thereafter can be exchanged by MnO$_4^-$-ions, leading to deposition of MnO$_2$ in the micropores, seems to require further evidence. Vacuum infiltration will only lead to wetting of the micropores by water, but neither SO$_4^{2-}$ nor MnO$_4^-$ will be able to enter the micropores without an external driving voltage. Therefore, by electroless deposition, as discussed in this study, MnO$_2$ will only be deposited on the external surface area of the carbon particles.

3.2.2. Variation of carbon particle size

To investigate the respective adsorption sites, in a second sample series we deposited MnO$_2$ on carbon xerogels of different particle sizes. The parameters for deposition were fixed at a concentration of 0.05 M NaMnO$_4$ and a deposition time of 4 h. These values were taken from the time- and concentration-dependent study, in which a high mass uptake of 35 wt.% MnO$_2$ together with a reasonable electrochemical performance could be achieved (see Figure 4(a), 4(b)).

The mass uptake for the S-, M- and L-samples, denoted as CXMn S, CXMn M, and CXMn L, respectively, is plotted as a function of the external surface area of the carbon backbone in Figure 6 (blue curve). Samples with small particles take up the largest amount of manganese oxide and vice versa the dependence on the external surface area $S_{\text{ext}}$ becomes obvious as the sample with the highest external surface area yields the highest mass uptake of MnO$_2$. However, the
ratio \( m_{MnO_2}/S_{ext} \) is not constant (Figure 6), as one would expect in case of a purely self-limiting process.

SEM micrographs of the small, medium and large carbon-MnO\(_2\) samples are shown in the lower row of Figure 1. No significant change in particle size can be detected on the resolved length scales when comparing the hybrid electrode to the corresponding carbon xerogel. Especially the well interconnected network of interparticular pores still remains open and accessible to electrolytic transport. The large particles (right image) seem to be textured on their surface, which may be related to a microstructured MnO\(_2\) coverage.

Via XPS measurements, samples of small and medium particle sizes proved to be chemically identical (see Figure 9(a), Supporting Information). A fit of the Mn2p\(_{3/2}\)-peak (see Figure 9(b), Supporting Information) reveals the manganese oxide in the electrode to be a mixture of Mn\(_2\)O\(_3\) and MnO\(_2\) at a ratio of 1:4.6. From this analysis we conclude the manganese oxide prepared in this study to consist preferentially of MnO\(_2\). The XPS analysis also hints for residual Na\(_2\)SO\(_4\) and Na\(_2\)SO\(_4\) in the samples. However, since all samples were processes by an identical route of preparation and in particular were subjected to the same washing procedure, the ratio of sodium sulfate- to manganese oxide-species can be assumed similar for all samples.

The gas sorption isotherms normalized to the total mass of the electrodes show a decrease in adsorbed volume which is of the order of the weight percentage of the deposited MnO\(_2\), namely 48, 29 and 3 wt.% for small, medium and large particles, respectively. Therefore, no substantial fraction of pore volume (detectable by N\(_2\) sorption) was secluded or filled with MnO\(_2\), rather the material is contributing to the sample mass only. In order to emphasize this effect more clearly, the isotherms normalized to the CX mass in the sample are plotted in Figure 2 and compared to the respective isotherms of the bare CX. For higher relative pressures the drop in the adsorbed volume differs significantly from the mass uptake, thus corresponding to a decrease of meso- and macropore volume in the course of MnO\(_2\) deposition on the external surface area of the carbon particles. This trend becomes also obvious in the calculated values of external
surface area $S_{\text{ext}}$ and the micropore volume $V_{\text{mic}}$ (see Table 1). The small particles show the biggest decrease (40 %) in $S_{\text{ext}}$, due to the fact that most of the MnO$_2$ was deposited on the external surface area of the carbon particles. As the pronounced decrease in micropore volume (64 %) can not only be attributed to a gain in mass, a significant number of micropores were either partially filled with MnO$_2$ or closed, hence are no longer accessible to N$_2$ molecules.

The calculated values (Table 1) from gas sorption data reveal an increase in $S_{\text{ext}}$ for all particle sizes if normalized to the mass of carbon xerogel in the sample. The external surface area shows a slight systematic increase, indicating additional changes of the microstructure induced by the MnO$_2$ deposit.

Supposed all mass of MnO$_2$ being deposited on the external surface area of the bare carbon xerogels, we can estimate the layer thickness $h$ by using a bulk density of $\rho_{\text{MnO}_2} = 5.026 \text{ g cm}^{-3}$ [35]:

$$h = \frac{m_{\text{MnO}_2}}{m_{\text{CX}}} \cdot \rho_{\text{MnO}_2}^{-1} \cdot S_{\text{ext}}^{-1}. \quad (4)$$

The resulting layer thickness is plotted vs. the external surface area in Figure 6 (red curve). As one can see, the samples with the largest particle size take up the least amount of MnO$_2$, however resulting in the thickest MnO$_2$-layer, of about 13 Å. This allows for two possible interpretations: The deposited MnO$_2$ mass was partially deposited as agglomerates within the carbon structure. SEM overview scans however do not show any irregularities in the carbon structure (see Figure 1). Therefore, an additional competitive deposition mechanism besides the previously proposed self-limiting process might lead to thicker deposits on the carbon surface area.

The cyclic voltammograms for the hybrid electrodes are displayed in Figure 3(b). For large particle sizes, the gain in gravimetric capacitance by MnO$_2$ pseudocapacitance is compensated by the gain in mass. In contrast, hybrid electrodes with medium and small particle sizes show an huge increase in capacitance while the corresponding CV curves still retain a rectangular shape, only marginally influenced by the reduced conductivity due to the MnO$_2$ layer formation. The bumps at about 0.1 V and 0.5 V vs. Ag/AgCl for samples com-
posed of medium and small particles in Figure 3(b) are an exclusive feature of the hybrid electrodes and have been attributed to ionic intercalation processes into MnO$_2$ upon charging [36].

In Figure 7(a) the gravimetric capacitance is plotted against the applied scan rate. Within the measured range, the capacitance of the carbon samples is less dependent on the scan rate compared to the hybrid electrodes. At 100 mVs$^{-1}$ the capacitance of the latter drops by 56 % for CXMn S and by 33 % for CXMn M. The reason for this behavior can be elucidated by comparing the CV-curves at the different scan rates, for instance for sample CXMn M, plotted in Figure 7(b). The rectangular shape at 2 mVs$^{-1}$ is increasingly disturbed at higher scan rates, mainly due to the decreasing slope at -0.3 V vs. Ag/AgCl. These observations can be attributed to the strong influence of the low conductive MnO$_2$ layer, both at the carbon-MnO$_2$-electrolyte interface and at the contact between the current collector and the carbon backbone.

Although the samples made of small particles the hybrid electrodes show a strong dependence of the capacitance on the scan rate, at 200 mVs$^{-1}$ the capacitance is still about 2 times higher than that of the bare carbon electrode.

4. Conclusion

Our study of the carbon-MnO$_2$ hybrid model system addresses the incorporation of MnO$_2$ into resorcinol-formaldehyde-derived carbon xerogels exhibiting different primary particle sizes and therefore different external surface area. A series of various infiltration times and concentrations showed no dependence on the preparation parameters for mass uptakes of MnO$_2$ up to 35 wt.%. For high mass uptakes, low concentrations of NaMnO$_4$ and long deposition times result in the largest capacitance increase by a factor of 3. By varying the size of the primary carbon particles in the xerogel, we demonstrated that deposition mainly takes place on the external surface area of the carbon backbone. Small backbone particles provide a higher specific external surface area and therefore can host more MnO$_2$ per mass of carbon xerogel than large particles.
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5. Tables

Table 1: Overview of structural data derived for the carbon xerogels as well as the corresponding hybrid xerogels. Mass specific values are normalized to the mass of carbon xerogel, the density \( \rho \) includes fibers and structural inhomogeneities in the electrodes.

| sample | wt.% | \( \rho \) [gcm\(^{-3}\)] | \( S_{\text{ext}} \) [m\(^2\)g\(^{-1}\)] | \( S_{\text{BET}} \) [m\(^2\)g\(^{-1}\)] | \( V_{\text{mic}} \) [cm\(^3\)g\(^{-1}\)] | \( d_{\text{part}} \) [nm] | \( d_{\text{pore}} \) [nm] |
|--------|-----|-----------------|-----------------|-----------------|-----------------|----------------|----------------|
| CX S   | 0   | 0.24±0.02       | 302±30          | 751±75          | 0.18±0.02       | 12±1           | 14±4           |
| CX M   | 0   | 0.16±0.02       | 74 ±7           | 601±60          | 0.21±0.02       | 53±6           | 108±31         |
| CX L   | 0   | 0.15±0.02       | 7 ±5            | 623±62          | 0.24±0.02       | 462±49         | 1184±355       |
| CXMn S | 48±4| 0.39±0.04       | 350±35          | 685±69          | 0.15±0.02       | –              | –              |
| CXMn M | 29±3| 0.25±0.03       | 78 ±8           | 528±53          | 0.18±0.02       | –              | –              |
| CXMn L | 3±1 | 0.21±0.02       | 1 ±5            | 610±61          | 0.24±0.02       | –              | –              |
6. Figures

Figure 1: SEM micrographs showing in the upper row the carbon backbone, consisting of small, medium and large particles (left to right). Carbon-Manganese-hybrid samples in the lower row show no significant change in structure.
Figure 2: N$_2$-gas sorption isotherms of carbon backbone (red) and hybrid samples (green) for three different particle sizes small (S), medium (M) and large (L), in Figures (a), (b) and (c), respectively. The data are normalized to the carbon xerogel mass without fibers and to standard temperature and pressure (STP).
Figure 3: Cyclic voltammogram at 2 mVs$^{-1}$ of bare carbon samples (full lines) with different particles sizes (a) and corresponding hybrid electrodes (dashed lines) (b).
Figure 4: (a) Mass percentage of MnO$_2$ deposition in the electrodes, plotted against the infiltration time for various concentrations of the NaMnO$_4$ precursor. Lines are guides to the eye. (b) Specific capacitance for hybrid electrodes as a function of the MnO$_2$ uptake. The bare carbon yields a capacitance of about 40 F/g. The dotted line shows a linear fit of the experimental data up to about 35 wt.% MnO$_2$. Errorbars are drawn exemplarily for the 0.10 M series.
Figure 5: CV curves for a bare carbon electrode CX and selected samples with a MnO$_2$ uptake of about 20 wt.% (a) and >50 wt.% (b), measured with a potential scan rate of 5 mVs$^{-1}$. 
Figure 6: MnO$_2$ wt.% (blue) and MnO$_2$-layer thickness $h$ (red) vs. external surface area. Error bars according to Table 1 for $S_{\text{ext}}$ and derived from Equation 4. The dotted lines serve as a guide to the eye.
Figure 7: (a) Gravimetric capacitance vs. applied scan rate, carbon samples (solid lines) and hybrid samples (dashed lines). (b) Cyclic voltammogram of sample CX Mn M for different scan rates.
Figure 8: **Supporting Information**: CV at different scan rates for sample CX L.
Figure 9: **Supporting Information:** Overview of XPS data, intensities normalized to the C1s peak and shifted for clarity: Pure carbon CX S and hybrid samples CXMn M, CXMn S (a). XPS-peak of Mn2p$^{3/2}$ for samples CXMn S and CXMn M (b), modeling of peaks according to [33][34]. The data for CXMn M was scaled by a factor of 2.1.
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