Switchable Supercapacitors with Transistor-Like Gating Characteristics (G-Cap)

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A novel three-electrode electrolyte supercapacitor (electric double-layer capacitor [EDLC]) architecture in which a symmetrical interdigital “working” two-electrode micro-supercapacitor array (W-Cap) is paired with a third “gate” electrode that reversibly depletes/injects electrolyte ions into the system controlling the “working” capacity effectively is described. All three electrodes are based on precursor-derived nanoporous carbons with well-defined specific surface area (735 m² g⁻¹). The interdigitated architecture of the W-Cap is precisely manufactured using 3D printing. The W-Cap operating with a proton conducting PVA/H₂SO₄-hydrogel electrolyte and high capacitance (6.9 mF cm⁻²) can be repeatedly switched “on” and “off”. By applying a low DC bias potential (−0.5 V) at the gate electrode, the AC electroadsorption in the coupled interdigital nanoporous carbon electrodes of the W-Cap is effectively suppressed leading to a stark capacity drop by two orders of magnitude from an “on” to an “off” state. The switchable micro-supercapacitor is the first of its kind. This general concept is suitable for implementing a broad range of nanoporous materials and advanced electrolytes expanding its functions and applications in future. The integration of intelligent functions into EDLC devices has extensive implications for diverse areas such as capacitive energy management, microelectronics, iontronics, and neuromodulation.

1. Introduction

Storing energy fast and repeatedly remains a major challenge at all scales, ranging from the large scale integration of renewable energy resources into the grid, to electric vehicles, autonomous systems and down to miniaturized devices and computing architectures.⁰⁻⁶ Completely autonomous micro-devices combine miniaturized components such as energy harvesters, converting for example mechanical, thermal, and solar energy, with micro-sensors and transmitting units. Energy storage units are decisive components of such self-powered devices compensating discontinuous energy harvesting and instabilities.⁶

Supercapacitors (electric double-layer capacitors, [EDLCs]) are established devices with moderate specific energy but high power density and ideal for short-term energy recovery.⁷ They are used for grid stabilization, brake energy recuperation and as intermediate buffer at all length scales ranging from large operating units with up to 1000 MW power down to a few μF capacitance in miniaturized micro-supercapacitors for miniaturized devices or bio-interfacing.⁷⁻¹¹ EDLCs using activated carbon as electrode material are based on physical charge storage mechanisms, storing energy via electrostatic charge separation on polarized electrodes enabling ultrafast charge and discharge rates and high power densities.¹²,¹³ Various carbon materials such as CDC,¹⁴⁻¹⁵ rGO,¹⁶,¹⁷ CNT,¹⁸⁻²⁰ graphene,²¹ and activated carbon²²,²³ have been used to ever boost the specific capacitance of such devices at material and device level. Recently, considerable efforts have promoted the miniaturization of 2D in-plane interdigital supercapacitors using top down approaches such as plasma etching,²⁸ direct laser writing,²⁹ or photolithographic techniques.²⁵ Furthermore also direct printing techniques (bottom up) were successfully applied providing a platform for manufacturing structured surfaces of carbon micro-structures using inkjet printing,²¹,²⁶,²⁷ soft lithography,²²,²₈ and 3D-printing.²⁹,³₀

While tremendous efforts have been devoted to boost the specific energy of such systems by material engineering, electrolyte development, and electrode structuring, the prevailing supercapacitor architecture is typically based on a symmetric cell-chargeable in two directions. However, a tremendous potential lies in the integration of more complex functionality into EDLC based devices as the highly reversible ion adsorption mechanism might enable the design of ion transistor architectures, in particular if the molecular species carry specific chemical information that delivers or regulates biological functions and processes. Such ion-based chemical circuits

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may be applicable to drug delivery, neuromodulation, or lead to neuromorphic devices.\cite{31–34} As a 1st generation device in this direction we have recently reported an ion-based supercapacitor diode (CAPode) with high rectification ratio via pore size engineering and an ion-sieving mechanism effectively blocking the negative bias charging direction.\cite{35}

In the following, we describe the 2nd generation of EDLC-based functional architectures, the first transistor analogue, a switchable micro-supercapacitor with high on/off ratio.

2. Results

Our architecture is based on a three-electrode device using a symmetric interdigital carbon electrode design as the AC operated supercapacitor (working supercapacitor, W-Cap) which is gated by a third thin film porous carbon gate electrode (G; Figure 1). In this concept, the third electrode (G) is used to control the EDLC charge storage capacity of the W-Cap by concurrent cation adsorption depleting the electrolyte concentration effectively. In this new assembly, the micro-supercapacitor (W-Cap) can be effectively switched “on” and “off” by applying an additional negative bias potential at the gate electrode. This 3-electrode architecture is termed “G-Cap” in the following.

2.1. Characteristics of the Prototypical G-Cap Design and Proof of the Concept

Our new concept of a gated supercapacitor is based on competing electroadsorption processes in a three-electrode supercapacitor device. A high performance working micro-supercapacitor (W-Cap) cycling with a defined specific capacitance is an essential component of the G-Cap architecture. Our interdigital W-Cap was produced via advanced 3D-printing of a liquid carbon precursor solution following a recently developed procedure (Figure S1, Supporting Information). This sucrose-derived nanoporous carbon requires no toxic solvents for processing and shows excellent electrical properties with well-defined surface areas (735 m² g⁻¹, Figure S2, Supporting Information). A proton conducting PVA/H₂SO₄-hydrogel electrolyte\cite{36} is used to achieve a high capacitance of 6.9 mF cm⁻² (10 mV s⁻¹) and an absolute capacitance of 2.4 mF. The W-Cap CV-curve has the expected rectangular shape (Figure 2a) with the expected decay at higher scan rates due to the limited mobility of the charge carriers in the gel electrolyte (Table 1). The W-cap shows an excellent charge–discharge cycling stability over 10 000 cycles (Figure S3, Supporting Information).

A key element of the new concept is a third nanoporous carbon “gate electrode” (G; Figure 1a,b) which allows to switch
the AC operated W-Cap “on” and “off” by applying a potential bias between working electrode and the G-electrode.

Before assembling the three-electrode G-Cap architecture we evaluated the G-electrode performance in a symmetric two-electrode setup (Figure 2b). We finally balanced this thin film G-electrode to provide a surplus of specific device capacitance (30.8 mF cm$^{-2}$ at 10 mV s$^{-1}$) and an absolute electrode capacitance of 10.7 mF (Table 1, Figure 2b) tailored to control the majority of charge carriers in the confined electrolyte reservoir in order to effectively switch “off” the W-Cap capacitance (Figure 1c). As long as G is not biased the W-Cap has a high device capacitance of 3.6 mF cm$^{-2}$ (1.3 mF, “on”). However, when G is polarized with negative bias the cations are immediately depleted in the electrolyte and the W-Cap capacitance decreases due to a deficit of charge carriers. They are no longer accessible for the electric double-layer formation and the W-Cap is effectively switched “off” (Figure 1c). In order to return back to the “on”-state of the W-Cap we enforce the reverse ion desorption at the bias G-electrode by a reverse bias pushing the ions back into the hydrogel and the W-Cap capacitance should recover to 100%.

Figure 3a shows the capacitance retention profile of one switching sequence. During the G-switching, the W-Cap is cycled continuously at a scan rate of 50 mV s$^{-1}$ between 0 and 0.5 V with a capacitance of 100%. After polarizing the bias electrode to −0.5 V the W-Cap capacitance rapidly decreases in the first three EDLC cycles and only delivers 1.8%, two orders of magnitude below the initial capacitance (Figure 3; Figure S4, Supporting Information). Moreover, with further cycling, the capacitance value remains stable and low. The latter is an outstanding result representing an excellent on/off ratio, in particular in consideration that this ion-based G-Cap is the first reported device of its kind far from being fully optimized. As we are using a proton conducting PVA/H$_2$SO$_4$-hydrogel electrolyte, a negative bias causes the depletion of protons, the main charge carriers in the W-Cap, to adsorb at the negatively charged G-electrode and hence the W-Cap is effectively switched “off”. According to our observations, after disconnecting the G-electrode the latter remains polarized. Complete desorption of protons from the nanoporous G-electrode and switching back, however, is achieved by applying a short positive bias of +1 V pushing the protons back into the electrolyte and the W-Cap capacitance returns to the initial “on” value of 100% after one cycle. The corresponding CV-curves of the different states are shown in Figure 3b. During cycling of the W-Cap at 50 mV s$^{-1}$ the CV-curves are rectangular indicating the absence of redox reactions. The CV-curve in the “off”-state is flat and the capacitive characteristics are effectively suppressed demonstrating a switchable supercapacitor for the first time. Moreover, after desorption of charge carriers from the G-electrode (“on”-state-2) the CV-curves perfectly superimpose the initial state demonstrating reversible on/off switchability. The highly reversible switchability of the G-Cap is shown in Figure 3c,d demonstrating the capacitance changes for ten on/off switching sequences applying a bias of −0.5 V in each sequence.

### 2.2. G-Cap Switching Characteristics

A key parameter controlling the switchability in our new architecture is the G-electrode bias potential. Hence, we studied the

| Scan rate [mV s$^{-1}$] | W-Cap Capacitance [mF] | Device capacitance [mF cm$^{-2}$] | Thin film (G-electrode) Capacitance [mF] | Device capacitance [mF cm$^{-2}$] |
|-------------------------|------------------------|-------------------------------|--------------------------------|-------------------------------|
| 5                       | 1.4                    | 3.9                           | 12.6                          | 36.0                          |
| 10                      | 1.3                    | 3.6                           | 10.7                          | 30.8                          |
| 20                      | 1.2                    | 3.4                           | 8.8                           | 25.2                          |
| 50                      | 1.1                    | 3.1                           | 5.9                           | 16.8                          |
| 100                     | 1.0                    | 2.8                           | 3.8                           | 10.7                          |
impact of bias-voltage by systematically varying the bias potential and monitoring the capacitance reduction after 5 min of applied bias. Figure 4a shows a characteristic exponential decay of the residual capacitance from 7% at a bias of $-5 \text{ mV}$ down to 1.8% at $-0.5 \text{ V}$. For positive bias potentials (Figure 4b) an exponential capacitance increase with rising bias potentials is observed. The gating characteristics are very comparable to that of a field effect transistor (FET) when plotting the drain current versus the gate–source voltage. In the given architecture a minimum gate voltage of approximately $-0.2 \text{ V}$ is sufficient to achieve a reasonable on/off ratio. As the PVA/H$_2$SO$_4$ hydrogel applied here is a proton-conducting polymer, the sulfate anions only play a minor role for switchability. The on/off switching is dominated by the proton depletion in the electrolyte at negative bias potentials. For an electrolyte with a higher anion contribution to the capacitive storage mechanism, we would expect reverse characteristics and a decreasing W-Cap capacitance for positive bias. The aqueous electrolyte limits the ideal voltage window for biasing. When off-switching is induced at higher positive bias potentials ($+1.2 \text{ V}$, Figure S5b,c, Supporting Information) the capacitance drops down to around 40% which is comparable to results obtained for smaller positive bias potentials (Figure 4b). Nevertheless, the system is stable during the on–off switching and parasitic redox reactions are not observed. Hence, off-switching with negative bias is more efficient for the acidic electrolyte and subsequent triggering of the desorption is achieved at $+1.0 \text{ V}$ or higher bias potential ($+1.2 \text{ V}$; Figure S5a, Supporting Information, 90% capacitance retention).

A second characteristic parameter is the scan rate of the W-Cap (Figure 4c). We varied the scan rates between 10 and 100 mV s$^{-1}$ at a bias potential of $-0.5 \text{ V}$ over 5 min (Figure 4d). Faster cycling at 100 mV s$^{-1}$ results in slightly decreased on/off ratios as compared to cycling at 50 mV s$^{-1}$. After 5 min equilibration, a capacitance retention of 3% is achieved which is only slightly higher than for the 50 mV s$^{-1}$ sequence. However, as the same number of cycles (3) is sufficient to achieve minimum capacitance, the faster cycling allows faster switching. Slow scan rates (10 or 20 mV s$^{-1}$) further increase the on/off ratio (1.3%) and higher overall capacitances of the W-Cap are achieved (Table 2). Here the switching takes place as fast as for the higher scan rates. For scan rates below 10 mV s$^{-1}$ parasitic redox reactions may negatively affect the performance.

The stability of repeated switching is proven during fast sequences at $-0.5 \text{ V}$ with off-state equilibration for 2.5 min. As shown in Figure 4e the complete capacitance reduction down to 6% is reproducible. By “on”-switching via proton desorption-push at $+1.0 \text{ V}$ for $30 \text{ s}$ the capacitance completely returns back to around 100%. Besides fast switching stability and cycling stability in the on-state, also the effect of resting for a longer time in the off-state was investigated. After switching the G-cap off at a bias of $-0.8 \text{ V}$ for $12 \text{ h}$ the on-switch is slightly retarded but
rapidly reaches a capacitance retention of 60%. After long off-state resting a pronounced kinetic hindrance of the desorption is observed and longer desorption intervals are required for operation, indicating typical hysteretic characteristics.

For reproducible operation of the switching device, we identified proper conditioning to be an essential requirement for high G-Cap performance. The latter is important in order to completely electro-wet the G-electrode and the W-Cap before operation. The nanoporous carbon material mainly contains micropores, and therefore various wetting sequences are needed to overcome diffusion limitations and pore blocking. In order to condition the G-electrode, the system is initially cycled in the “off”-state at a bias potential of $-1.2\,\text{V}$. Overall three sequences (10 min adsorption and 30 s desorption) are performed until the minimum capacitance is reached with fast switching behavior. These higher bias potentials are crucial to maximize the G-electrode efficiency by electrowetting. In order to demonstrate the importance of preconditioning we analyzed several electrowetting sequences (Figure 5) clearly demonstrating improved switching kinetics with increasing number of pretreatment cycles. The conditioning significantly reduces the minimum bias required to achieve a high on/off ratio. Moreover, parasitic redox reactions originating from cell polarization are minimized as the G-Cap can be operated at lower bias potentials (equivalent to gate voltage).

### 3. Conclusion

A novel switchable supercapacitor (G-Cap) architecture was presented for the first time. By matching a two-electrode working micro-supercapacitor with a larger third nanoporous gate electrode, capacitance switching by electrolyte depletion is achieved between “on” (100%) and “off”-states (1.8%) reversibly with high capacitance regeneration. The purely physical ion adsorption enables fast and repeated switching characteristics without degeneration. Varying the gate voltage reveals an exponential capacitance decay with decreasing gate-bias comparable to those of FET transistors. In this sense, G-Caps may be regarded as AC analogues of semiconductor-based

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**Table 2.** G-Cap capacitances switching characteristics (on/off ratios) at varied scan rates.

| Scan rate [mV s$^{-1}$] | Capacitance [F] | Capacitance [F] | Capacitance retention [%] |
|-------------------------|-----------------|-----------------|---------------------------|
|                         | “on”-state      | “off”-state (-0.5 V, 5 min) | “off”-state (-0.5 V, 5 min) |
|---|---|---|---|
| 10 | $1.21 \times 10^{-3}$ | $1.61 \times 10^{-5}$ | 1.3 |
| 20 | $8.68 \times 10^{-4}$ | $1.12 \times 10^{-5}$ | 1.3 |
| 50 | $3.79 \times 10^{-4}$ | $7.61 \times 10^{-6}$ | 2.0 |
| 100 | $1.65 \times 10^{-4}$ | $4.93 \times 10^{-6}$ | 3.0 |

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**Figure 4.** G-Cap characteristics: a,b) capacitance retention at 50 mV s$^{-1}$ after bias application and equilibration, c) capacitances at varying scan rates (blue triangles: switched-on-state, black dots: switched off after 5 min at $-0.5\,\text{V}$ bias), d) typical capacitance retention for one switching sequence (on–off–on) at 50 mV s$^{-1}$ (black) and 100 mV s$^{-1}$ (blue), and e) capacitance retention during fast cycling (50 mV s$^{-1}$) using a gating bias of $-0.5\,\text{V}$ for 2.5 min.
transistors with intrinsic capability for energy or chemical information storage. The G-Caps gate-voltage dependent capacity characteristics resembling typical FET gate-voltage-current are remarkable and may stimulate more detailed mechanistic analyzes in future. However, an in depth simulation is beyond the scope of this initial proof-of-concept demonstration. Prospective chances lie in the integration of pore-size engineered carbons, selective membranes, and organic electrolytes. Precise pore size engineering may lead to selective ion-sieving.[35] Organic electrolytes offer a much wider voltage window.[37] Ionic conductivity and transfer number are decisive factors for tailoring G-Cap performance in future. The acidic electrolyte seems to mask anionic involvement effectively. More complex systems could be used to tailor current–voltage characteristics through ion mobility and their capacitive contribution. More complex systems could be used to tailor current-voltage characteristics through ion mobility and their capacitive contribution. Further investigations in this direction are promising for achieving a wider range of G-Cap operation windows and rates. We consider G-Caps as 2nd generation EDLC-based devices providing the required functionality for advanced ion-based computing architectures and switchable devices. In particular, in combination with EDLC-based diode analogues of the 1st generation (CAPodes) more complex logic gates (AND, NAND etc.) may be envisioned. Balancing the G-electrode, pore size engineering, and adaption to the electrolyte provides essential means of tuning the performance of the G-Cap in future. Important insights into ion diffusion and electroadsorption mechanisms may be achieved by selectively analyzing the adsorption kinetics of electrolyte ions, complex biomolecules, or even neurotransmitters. The ultrahigh capacitance of supercapacitors and the ability to electrosorb even complex biological macromolecules by tuning pore size and surface functionality render G-Caps as promising devices for neuromodulation, drug delivery, and ion transistor circuits.

4. Experimental Section

Precursor and Electrode Preparation: The sucrose precursor was prepared as described by Lochmann et al.[22] For the 3D-printing 1 mL of the precursor was additionally diluted with 3.7 mL deionized water and 0.5 mL ethanol. Carbon thin films for the G-electrode were prepared via spin coating on silicon wafer (25 × 10 mm). Prior to the coating process, the wafers were cleaned in ethanol and activated in an Ar-plasma (Knippen, Neoplas Tools). 20 μL of the highly concentrated sucrose precursor were applied on the substrate and spin coating (Spin 150, ATP GmbH) was performed with 2000 rpm for 30 s. The films were then dried at 120 °C and carbonized at 900 °C for 2 h (heating rate 150 K h⁻¹).

3D-printed interdigital structures of the W-Cap were prepared using a BioScaffold 3.2 (GeSim mbH). The structures were printed on boro-aluminum silicate substrates (25 × 25 mm, Corning 1737, DELTA Technologies) which were activated in piranha solution (1 part H₂O₂ and 3 parts conc. H₂SO₄) and washed with deionized water and ethanol. Before printing, the substrates were heated to 120 °C and printing was carried out at around 80 °C. Defined droplets were adjusted using a stroboscopic camera. Separated precursor droplets were produced at a frequency of 150 Hz, a pulse width of 90 μs and a voltage of 55 V. The post-treatment is identical to that for the thin films.

Electrochemical Characterization: The interdigital carbon electrodes of the W-Cap were contacted with silver conducting paste (Ferro GmbH) on the contact pads. Furthermore, an area of 5 × 7 mm around the electrode was taped with Kapton foil and a Kapton spacer of 0.3 mm was placed on top to define the reservoir for the electrolyte. Afterward the electrode was activated in an Ar-plasma and 60–90 μL PVA/H₂SO₄ hydrogel electrolyte was applied on it. The carbon thin film electrode was also masked with a 5 × 7 mm ring of Kapton foil and activated in Ar-plasma. Subsequently, it was pressed onto the spacer to form a sandwich type setup. For comparison, also two carbon films were taped and assembled with a spacer and electrolyte.

Symmetric supercapacitors were analyzed using a Biologic VMP-3 potentiostat in a two electrode setup. Cyclic voltammetry was measured with scan rates of 5–100 mV s⁻¹ in a voltage range of 0–0.5 V. The G-Cap was tested in a CE to ground setup synchronizing two ports with a combined working electrode. Cyclic voltammetry during the switching process between W-Cap and G-Cap was carried out in a voltage range between 0–0.5 V and a bias between −1.5 and 1.5 V was applied using chronoamperometry.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

3D printing, gating, micro-supercapacitors, nanoporous carbon, supercapacitors

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