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Lithium-ion capacitors using carbide-derived carbon as the positive electrode – A comparison of cells with graphite and Li$_4$Ti$_5$O$_{12}$ as the negative electrode

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Abstract

The use of carbide-derived carbon (CDC) as the positive electrode material for lithium-ion capacitors (LICs) is investigated. CDC based LIC cells are studied utilizing two different negative electrode materials: graphite and lithium titanate Li$_4$Ti$_5$O$_{12}$ (LTO). The graphite electrodes are prelithiated before assembling the LICs, and LTO containing cells are studied with and without prelithiation. The rate capability and cycle life stability during 1000 cycles are evaluated by galvanostatic cycling at current densities of 0.4–4 mA cm$^{-2}$. The CDC shows a specific capacitance of 120 F g$^{-1}$ in the organic lithium-containing electrolyte, and the LICs demonstrate a good stability over 1000 charge-discharge cycles. The choice of the negative electrode is found to have an effect on the utilization of the CDC positive electrode during cycling and on the specific energy of the device. The graphite/CDC cell delivers a maximum specific discharge energy of 90 Wh kg$^{-1}$ based on the total mass of active material in the cell. Both the prelithiated and non-prelithiated LTO/CDC cells show a specific energy of around 30 Wh kg$^{-1}$.

Keywords: Carbide-derived carbon; Lithium titanate; Graphite; Hybrid supercapacitor; Lithium-ion capacitor; Asymmetric capacitor

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1. Introduction

Electrochemical double-layer capacitors (EDLCs) are one of the most promising power storage technologies at the moment. They store energy through charge separation and the formation of an electrical double layer at the interface between a high surface area carbon electrode and the electrolyte solution. Since there is no charge transfer through the electrode-electrolyte interface, the charge storage mechanism is fast, and thus high power devices can be produced. However, the major drawback of present-day EDLCs is their relatively low specific energy (around 5 Wh kg\(^{-1}\)) compared to rechargeable batteries (20–200 Wh kg\(^{-1}\)). [1–3]

The amount of energy stored in an EDLC is proportional to the capacitance, \(C\), and the square of the operating voltage, \(U^2\), according to equation \(E = (1/2)CU^2\). Thus, one approach to increase the energy density is to maximize the charge storage capability of the capacitive electrodes of the EDLC, typically made of activated carbons. [1] In recent years, nanoporous carbide-derived carbons (CDCs) [4] have gained more attention, especially as promising electrode materials in energy storage applications [5]. The uniqueness of CDC materials lies in the narrow pore size distribution, which can be controlled during the carbon manufacturing process [6]. Therefore, the pores of CDC are easily adopted to match the size of the electrolyte ions and to achieve the most effective usage of the carbon surface for adsorbing the electrical charges from the electrolyte. For example, in common organic electrolytes (e.g., NR\(_4^+\) BF\(_4^-\) in non-aqueous solvent), the nanoporous CDC with a pore size of \(~0.8\) nm has revealed an excellent capacity of both, cations (NR\(_4^+\)) and anions (BF\(_4^-\)), providing a capacitance of as high as 81 F cm\(^{-3}\) and 93 F cm\(^{-3}\) at negative and positive potential values, respectively [7].

Another effective approach to increase the energy density is to increase the operating voltage of the EDLC. One method to do this is by replacing the organic electrolyte with an ionic liquid which has a wider electrochemical stability window. However, ionic liquids in energy storage applications suffer from low conductivity at room temperature, high viscosity and high price. [1] Another method is via replacing one of the capacitive carbon electrodes with a ‘battery-like’ faradaic electrode to form an asymmetric hybrid supercapacitor. If the faradaic electrode is composed of a lithium intercalation material, the asymmetric cell is called a lithium-ion capacitor (LIC). During the charging/discharging of a LIC, two distinct energy storage mechanisms take place: the adsorption/desorption of ions in the electrical double layer on the surface of the capacitive electrode and insertion/extraction of lithium ions within the bulk of the battery-like electrode.
Amatucci et al. in 2001 [8] were among the first to report on the development of a prototype LIC. Their cell utilized a lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$, LTO) negative electrode combined with an activated carbon positive electrode. It exhibited a packaged gravimetric energy density of 11 Wh kg$^{-1}$ [9] which corresponded to a three to five times increase compared to conventional EDLCs at the time. Since then, LTO has become one of the most frequently reported negative electrode materials for LICs in the literature [10–17]. One of the benefits of using LTO as the negative electrode is its negligible volume change during lithium insertion/extraction, enabling a long cycle life for the LIC. In addition, the lithium-insertion voltage of LTO (1.55 V vs. Li/Li$^+$) is relatively high and inside the stability window of commonly used organic electrolytes, which indicates that no passivating solid electrolyte interface (SEI) layer is formed on the surface of LTO. [18] This is beneficial for a LIC, since a resistive SEI layer could limit the power performance of the device. Furthermore, the choice of the electrolyte is not limited by its SEI-forming ability, and electrolytes with high conductivities can be used. The drawback of the high operating potential of LTO, however, is that the maximum cell voltage of the LIC will remain rather low, around 2.8 V. [9,16]

Another popular choice for the negative electrode has been carbonaceous materials either in graphitic form or as hard or soft carbons [19–31]. They provide cell voltages as high as 3.8–4.0 V (vs. activated carbon) [16] and thus a higher specific energy compared to LTO. Moreover, graphite is a traditional negative electrode material in lithium-ion batteries, which makes it a natural choice for the negative electrode of the LIC as well. For example, Khomenko et al. [20] prepared a LIC using a natural graphite negative electrode combined with an activated carbon positive electrode and obtained a specific energy of over 100 Wh kg$^{-1}$ (the value is given per masses of the electrodes and corresponds to a packaged gravimetric energy density of roughly 30–40 Wh kg$^{-1}$, depending on the packaging [32,33]). A disadvantage of using graphite as the negative electrode is that its operating potential lies outside of the stability window of the common organic electrolytes, and consequently, SEI-layer formation will occur on its surface.

To compensate for the loss of lithium ions from the electrolyte due to SEI-layer growth, graphite electrodes should be prelithiated prior to the use as the negative electrode in a LIC. Several studies have reported various ways to prelithiate the carbonaceous negative electrode to the desired state of charge (SOC). These methods include, for example, utilizing an auxiliary metallic lithium electrode assembled as the third electrode in the cell [19,21] or applying stabilized lithium-metal powder directly on the surface of the negative electrode prior to cell assembly [25–27]. By prelithiating the
graphite electrode, its operating potential can also be controlled to the desired value at around 0.1 V vs. Li/Li+. While this low potential enables the higher specific energy of graphite-based LICs, it also introduces a risk of lithium plating when charging at high currents or at low temperatures, thus reducing the safety of the cells.

As the negative electrode of the LIC undergoes a faradaic intercalation reaction during the operation of the cell, its performance will be sluggish compared to the positive electrode with a capacitive energy storage mechanism. Therefore, the power performance of the LIC is limited by the kinetics of the lithium-intercalation reaction on the negative electrode. On the other hand, since the capacitive process on the positive electrode occurs only on the surface of the high surface area carbon (unlike the intercalation reaction which occurs in the bulk of the negative electrode), the capacity of the LIC is controlled by the positive electrode. [34,35] Consequently, new materials with higher specific capacitance values to replace the commonly used activated carbons have been searched for. However, the investigations of positive electrode materials for LICs have been rather scarce to date. The studied materials reported in the literature include, for example, conducting polymers [11], activated graphene [33,36], carbon nanotubes [37] and composite materials combining both capacitive and faradaic materials in one electrode [14].

In this work, we propose the use of nanoporous CDC as the positive electrode for LICs. The performance of the material is studied by combining the CDC in LIC cells with two traditional negative electrodes: graphite and LTO. The characteristics and performance of both cell chemistries are reported, and the effect of the negative electrode material on the operation and utilization of the CDC positive electrode is discussed. In the majority of the experiments, the LTO electrode is prelithiated similarly to the graphite electrode, but brief tests with non-prelithiated LTO electrode are performed as well, and the consequences of omitting the prelithiation step are discussed.

2. Experimental

2.1 Preparation of the nanoporous CDC
The nanoporous CDC was produced from titanium carbide powder by using the common chlorination method. For that, TiC powder (H.C. Starck, average particle size < 4µm, 25g) placed in a quartz-boat was reacted by a flow of chlorine gas (AGA, 2.8) in a horizontal quartz bed reactor at 900 °C. The by-product, TiCl₄, was led away by the stream of the excess chlorine and neutralized by an alkaline solution. During heating and cooling, the reactor was flushed with a slow stream of argon. After complete removal of titanium from the carbide, the CDC was transferred to another quartz tube reactor and post-treated with hydrogen (AGA, 4.0) at 800 °C to deeply dechlorinate the CDC powder and to deactivate the dangling bonds remaining after the chlorination procedure. The CDC, with a final yield of 95% from theoretical, was characterized by using low-temperature N₂ adsorption measurements at 77K. Specific surface area, calculated according to Brunauer-Emmett-Teller (BET), was 1460 m² g⁻¹. Total pore volume, measured close to saturation pressure (P/P₀ = 0.95), was 0.69 cm³ g⁻¹ and the volume of micropores according to t-plot was 0.61 cm³ g⁻¹.

2.2 Preparation of the electrodes

The CDC electrodes were produced from a mixture of 90 wt% CDC powder and 10 wt% polytetrafluoroethylene binder (PTFE, Aldrich, 60 wt% suspension in water), which was cold-rolled stepwise into the carbon film with a final thickness of 150 ± 5 µm. The average active material loading of the CDC electrodes was 10.5 mg cm⁻². An aluminum foil with a conductive carbon coating was used as the current collector for the free-standing electrodes.

The preparation of the graphite electrode slurry was started by dissolving sodium carboxymethylcellulose (CMC, Bondwell™, Ashland) in deionized water. Then, carbon black (Super C65, Imerys) and the graphite powder (artificial type, BTR New Energy Materials) were added, and the slurry was mixed with a dispergator mixer. In the final stage of mixing, styrene-butadiene rubber (SBR, BASF, 50 wt% suspension in water) was added as the binder. The slurry composition was 94.3 wt% graphite, 2.8 wt% SBR, 1.4 wt% CMC and 1.4 wt% carbon black. The graphite slurry was coated on a copper foil using doctor blade technique with a wet thickness of 190 µm and dried at 60 °C for 20 min. The average active material loading of the graphite electrodes was 9.6 mg cm⁻². Samples of 18 mm in diameter were cut from the electrode sheets and calendared with a pressure of 0.3 t cm⁻².
The LTO slurry was produced by first dissolving polyvinylidene fluoride (PVDF, Solef 5130, Solvay) in N-methylpyrrolidone (Micropure™, Ashland/Life Science, BASF). Then, carbon black (Super C65, Imerys) and the LTO active material powder were added, and the slurry was mixed with a dispergator mixer. The tested electrode material was a commercial Li₄Ti₅O₁₂ powder (T2, Clariant, specific surface area 7 m² g⁻¹) and the slurry composition was 91.7 wt% LTO, 4.6 wt% PVDF and 3.7 wt% carbon black. The LTO slurry was applied on an aluminum foil using doctor blade technique with a wet thickness of 80–220 µm. The coated foils were first dried at room temperature overnight and then in an oven at 60 °C for 4 h. The average active material loading of the LTO electrodes was 11.1 mg cm⁻² in the prelithiated LTO/CDC cells and 4.3 mg cm⁻² in the non-prelithiated LTO/CDC cells. Samples of 18 mm in diameter were cut from the electrode sheets and calendared with a pressure of 2.0 t cm⁻².

### 2.3 Test cell assembly

The calendared electrodes and the test cell parts were first dried at 100 °C under vacuum for at least 20 h. Then they were transferred under vacuum into an argon-filled glove box (Jacomex, oxygen and water vapor levels below 1 ppm) where the cells were assembled. Electrochemical tests were performed in commercial 18 mm test cells (EL-CELL). Two-electrode setup was used to characterize the energy densities of the cells, whereas three-electrode setup was utilized to monitor the individual potentials of the positive and negative electrodes during charging and discharging. The reference electrodes in the LICs were metallic lithium (Aldrich). A glass fiber separator (EL-CELL) of thickness 1.55 mm was used for the three-electrode measurements and 0.26 mm for the two-electrode setup. The electrolyte solution consisted of 1 M LiPF₆ (lithium hexafluorophosphate) salt in a quaternary mixture of ethylene carbonate and other common organic carbonates.

To study the electrochemical stability window of the electrolyte solution in contact with high surface area carbon, symmetric cells with activated carbon were assembled. The cells contained either the carbonate based electrolyte or a more typical EDLC electrolyte, 1.8 M TEMA-BF₄ (triethylmethylammonium tetrafluoroborate) in acetonitrile (AN). In these cells, an activated carbon quasi-reference electrode was used, since the acetonitrile electrolyte is not stable at the potential of a lithium-metal reference electrode [35,38].
2.4 Prelithiation and electrochemical measurements

All of the electrochemical tests were carried out at room temperature. Prelithiation of the negative electrodes was performed in the EL-CELL test cells in a two-electrode setup against a lithium-metal counter electrode. The cells were first charged and discharged once at a low current rate of 0.02C (C-rate calculated based on the active material mass of the electrodes and the theoretical capacity of LTO, 175 mAh g⁻¹, and graphite, 372 mAh g⁻¹) to determine the actual capacity of the electrodes which was then used for the precise adjustment of the SOC. The graphite electrodes were prelithiated to a SOC of 37.5 % and the LTO electrodes were prelithiated to 50.0 % SOC. After the adjustment of the SOC, the cells were carefully disassembled inside the argon-filled glove box, and the prelithiated negative electrodes were transferred to another test cell with fresh electrolyte and the CDC positive electrode. Charging and discharging experiments were conducted using a Maccor 4300 battery testing station. Cyclic voltammograms (CV) were recorded using a Metrohm Autolab potentiostat (PGSTAT302N). The voltage cut-off limits applied during the electrochemical measurements of the LICs are presented in Table 1. The currents used during the cycling of the cells are presented in Table 2 where the current densities applied to the cells are presented together with the corresponding currents per active material mass on the positive electrode and the C-rates for the negative electrode. The balancing of the cells was done so that the active material loading of the CDC positive electrode was constant throughout the experiments, and the mass loading of the negative electrode was varied according to the material used.

|                     | Graphite/CDC | LTO/CDC | NPL-LTO¹/CDC |
|---------------------|--------------|---------|--------------|
| Charge cut-off voltage [V] | 4.0          | 2.55    | 2.55         |
| Discharge cut-off voltage [V]  | 2.0          | 1.55    | 1.65         |

¹ Non-prelithiated LTO
Table 2. The current densities applied to the cells during the charging/discharging of the LICs and the corresponding currents per active material mass on the positive electrode and C-rates for the negative electrode.

| $i_{\text{cell}}$ (mA cm$^{-2}$) | $i_{\text{CDC}}$ (mA g$^{-1}$) | C-rate (graphite) | C-rate (LTO) | C-rate (NPL-LTO) |
|---|---|---|---|---|
| 0.4 | 35–40 | 0.1 | 0.2 | 0.5 |
| 2 | 180–190 | 0.5–0.6 | 1.0 | 2.6 |
| 4 | 365–375 | 1.1 | 2.0 | 5.2 |

The specific energies were determined from the constant current cycling tests using the area under the discharge curve according to equation (1)

$$E_{\text{sp}} = \frac{i}{m_{\text{active}}} \int U \, dt_d$$

where $I$ is the current, $U$ is the cell voltage, $t_d$ is the discharge time and $m_{\text{active}}$ is the total amount of active material (CDC/LTO/graphite) in the positive and negative electrodes including the predoped lithium but excluding the masses of the cell casing, separator, current collectors, binder materials, conductive carbon and electrolyte. The mass of the predoped lithium was calculated from the half-cell charge-discharge data using Faraday’s law. The integral refers to the area between the highest and lowest voltage values during discharge. [39]

The capacitance of a LIC can be presented as a serial connection of the capacitances of the positive and negative electrodes as follows

$$\frac{1}{C} = \frac{1}{C_p} + \frac{1}{C_n}$$

(2)

According to eq. (2), the total capacitance of the LIC is controlled by the smaller of the two components. The capacitance of the faradaic electrode can be taken to be infinite compared to the capacitive electrode [34]. Thus, the measured capacitance of the LIC is here taken to represent the capacitance of the CDC positive electrode in the cell.
Accordingly, the specific capacitance, \( C_{SP} \), values for the CDC were calculated from the constant current discharge curves of the LICs using equation (3)

\[
C_{SP} = \frac{I}{\frac{dU}{dt} \ m_{CDC,active}}
\]  

(3)

where \( m_{CDC,active} \) is the mass of CDC in the positive electrode and \( \frac{dU}{dt} \) is the slope of the discharge curve in the range from 0.95\( U_{\text{max}} \) to 0.80\( U_{\text{max}} \). \( U_{\text{max}} \) is the charge voltage cut-off limit as defined in Table 1 for the different cell types. This voltage range corresponded to the linear part of the discharge curves.

The specific capacity of the CDC material depends linearly on the specific capacitance and the applied voltage window (\( \Delta U \)) and was calculated using equation (4)

\[
Q_{SP} = C_{SP} \Delta U
\]  

(4)

3. Results and Discussion

3.1 Determination of the usable voltage windows of the LICs

The energy density of a LIC depends on its operating voltage. Thus, to improve the energy density, the maximum voltage of the cell should be as high as possible. However, a high cell voltage may compromise the stability of the positive electrode-electrolyte interface. It has been shown that oxidative side reactions and anion intercalation may occur on the surface of even relatively low surface area carbons in organic lithium-containing electrolytes at potentials over 4.6 V vs. Li/Li\(^+\) [40,41]. In addition, it has been suggested by Zheng et al. [40] that increasing the surface area of the carbon could lower the onset potential of the oxidative side reactions due to an increased number of oxygen functional groups on the carbon surface. Hence, to estimate the maximum usable voltages of the LICs, the electrochemical stability window of the lithium-containing electrolyte in contact with high surface area carbon was studied.
A symmetric cell with activated carbon as both the positive and negative electrodes and 1 M LiPF₆ in a mixture of carbonates as the electrolyte was assembled. A commercially available activated carbon powder was chosen for the pretesting due to a better availability compared to the CDC. A CV recorded in three-electrode configuration against an activated carbon quasi-reference electrode (AC QRE) is shown in Fig. 1. For comparison, the CV of a cell with a more typical EDLC electrolyte, 1.8 M TEMA-BF₄ in acetonitrile (AN) solvent, is also shown in Fig. 1. The CVs with both electrolytes in Fig. 1 display a butterfly shape typical for capacitive materials. It can be seen that oxidative decomposition of the lithium-containing electrolyte starts to take place at potentials in the range of 1.0–1.2 V vs. AC QRE. In the negative end of the CVs, in turn, no significant electrolyte reduction is detected in the studied potential window. The products of the oxidation reaction could limit the access of the electrolyte to the carbon surface, thus reducing the specific capacitance and increasing the impedance of the cell [35]. Therefore, to prevent the oxidation of the electrolyte, the upper limit of the potential window of the positive electrode should be adjusted to values below the onset of the oxidation reaction. Thus, the upper limit of the CDC potential in the LICs was set to 1.0 V above the immersion potential (the immersion potential corresponds to 0 V vs. AC QRE in Fig. 1). The open circuit voltage of the LIC measured after assembling the cell prior to any other measurements represents the immersion potential of CDC against the studied negative electrode. The potential of the negative electrode can be assumed to remain roughly constant during the cycling of the LIC. Therefore, the upper limits of the voltage windows of the LICs were adjusted to 1.0 V above the open circuit voltage of a freshly assembled cell which was approximately 3 V for the graphite/CDC cell and 1.55 V for the LTO/CDC cell. The corresponding charge cut-off voltages were 4.0 V for the graphite/CDC cell and 2.55 V for the LTO/CDC cell. The choice of the lower limit for the voltage window will be discussed separately for each of the cell chemistries in Sections 3.2, 3.3 and 3.4.
Fig. 1. CVs (1 mV s⁻¹) of symmetric activated carbon cells measured in a three-electrode setup with an electrolyte consisting of 1 M LiPF₆ salt in a quaternary mixture of ethylene carbonate and other common organic carbonates (solid line) and 1.8 M TEMA-BF₄ in acetonitrile (dashed line).

3.2 LIC with prelithiated graphite as the negative electrode

Before assembling the LICs, the potential characteristics of the electrode materials were studied against lithium metal. The potential profile of the graphite electrode during a charge-discharge cycle at a rate of 0.02C is presented in Fig. 2. The graphite electrode shows the typical staging behavior in which the potential changes as a function of the SOC in a stepwise manner. The staging is related to the reaction mechanism of lithium intercalation into graphite. The lithium ions fill the gaps between graphene layers in an ordered way, and regular numbers of unoccupied layer gaps are formed between the occupied layers. The intercalation phases can be described with a stage index which describes the number of graphene layers between two lithium layers. The plateaus seen in the graphite potential correspond to two-phase regions where two different stage intercalation phases coexist, whereas the single-phase areas are seen as changing potential as a function of SOC. [42,43]
Fig. 2. The potential profile of the graphite electrode as a function of SOC during a charge-discharge cycle at 0.02C. The SOC range of the graphite electrode that was utilized during the charging/discharging of the graphite/CDC LIC is also indicated in the figure. The graphite electrode was prelithiated to 37.5 % SOC.

For the LIC, it is desirable that the potential of the negative electrode remains at a constant, low potential value during cycling. This maximizes the cell voltage and enables the use of a wide potential range on the positive electrode. Thus, the charge balancing of the graphite/CDC cell was implemented so that, during the cycling of the LIC, the range of SOCs of the graphite electrode was narrow enough to remain inside one of the two-phase regions showing a constant potential as a function of SOC.

The charge balancing of the graphite/CDC cell was calculated using the measured specific capacity of the CDC and the theoretical capacity of graphite (372 mAh g\(^{-1}\)). The specific capacitance of the CDC in the lithium-containing electrolyte was roughly 120 F g\(^{-1}\) (Fig. 3) which corresponds to a specific capacity of 33.3 mAh g\(^{-1}\) V\(^{-1}\). A voltage window of 2.0 V (from 2.0 V to 4.0 V) was applied during the cycling of the graphite/CDC cell, and in this range the capacity of the CDC was 66.6 mAh g\(^{-1}\). The positive to negative electrode mass ratio chosen for the graphite/CDC LIC was approximately \( r = 1.1 \) (\( r = m_{\text{CDC,active}}/m_{\text{graphite,active}} \)). With this mass ratio, the capacity of the CDC electrode corresponded to roughly 20 % of the theoretical capacity of the graphite electrode.

Although using an excess of capacity at the graphite electrode decreases the gravimetric energy density of the device, it also improves the power performance which is limited by the kinetics of the graphite electrode, as stated in Section 1. Thus, using an excess of the graphite material in the LIC is necessary, as good power performance is essential for the technology. Moreover, other authors
have ended up using a similar balancing of the electrodes after the optimization of the device performance [20].

![Graph of potential profile of the CDC electrode](image)

Fig. 3. The potential profile of the CDC electrode measured at 20 mA g$^{-1}$ in the lithium-containing electrolyte against a lithium-metal electrode.

Prior to assembling the LIC, the graphite electrode was prelithiated to a SOC corresponding to 37.5% of the measured capacity of the electrode. At this prelithiation level, the graphite electrode operated in the potential plateau of the stage-3–stage-2 two-phase region at 22–50% SOC during the cycling of the LIC (Fig. 2). It has been shown by Sethuraman et al. [44,45] that in this SOC range, the stress developed in the graphite material due to lithium intercalation and deintercalation is stable. Moreover, Zhang et al. [28] have studied the effect of the degree of prelithiation on the performance and stability of graphitized mesocarbon microbead/activated carbon LICs. They found that prelithiation levels corresponding to the graphite potential plateaus at 80 mV vs. Li/Li$^+$ (at SOC 50–100%) and at 130 mV vs. Li/Li$^+$ (SOC 22–50%) both yield LICs with high gravimetric energy and power densities as well as stable performance [28]. However, when the SOC range of the graphite electrode is limited inside the potential plateau at 130 mV vs. Li/Li$^+$, there is also a wider safety window against lithium plating on the graphite surface. Thus, it was chosen for the graphite-based LIC in this study.

A graphite/CDC LIC was assembled and a lithium-metal reference electrode was placed in the cell to record the potentials of the positive and negative electrodes during cycling. A CV measured for the cell showed that the potential of the graphite electrode remained roughly constant inside the voltage plateau at 22–50% SOC during the charging/discharging of the cell. Moreover, no
considerable oxidation of the electrolyte took place on the CDC electrode when the cell voltage was limited to 4.0 V (Fig. S1 in the Supplementary data). Fig. 4a shows the cycling stability of the graphite/CDC cell at a current density of 2 mA cm\(^{-2}\) when cycled between 2.0 V and 4.0 V. The fluctuations seen in the specific energy and energy efficiency are caused by small variations in the room temperature. The cell performance was stable: it showed an energy retention of 98.0 % after 1000 charge-discharge cycles. A specific energy density of 65.5 Wh kg\(^{-1}\) was obtained at 2 mA cm\(^{-2}\), and the energy efficiency was over 89.9 % throughout the cycling. Also, the coulombic efficiency remained above 99.7 % during the test. It should be noted here that the separator used in the three-electrode cell was quite thick, 1.55 mm, and therefore the voltage loss caused by the cell resistance was high during these measurements, leading to a lower specific energy. Measurements done using a thinner separator causing a lower cell resistance are reviewed in Section 3.5.

The potential profiles of the CDC positive electrode and the graphite negative electrode together with the cell voltage profile during the 1\(^{\text{st}}\) and the 1000\(^{\text{th}}\) cycle are presented in Figs. 4b and 4c. During the 1\(^{\text{st}}\) cycle, the graphite electrode potential swung in a 0.35 V window between end values of -0.04 V and 0.31 V vs. Li/Li\(^+\), and the CDC potential swing was 1.65 V between the values 2.30 V and 3.95 V vs. Li/Li\(^+\). As stated earlier, in order to maximize the capacity of the CDC electrode, the potential swing of the positive electrode should be as wide as possible in the cell voltage window (Eq. (4)). To enable this, the potential of the negative electrode should remain approximately constant. Therefore, a potential swing of 0.35 V on the negative electrode indicates that the capacity of the CDC cannot be utilized optimally at the studied current density. During the 1000\(^{\text{th}}\) cycle, the potential swing of the graphite electrode was still 0.34 V, and its potential had increased very slightly to values between -0.02 V and 0.32 V vs. Li/Li\(^+\). The width of the CDC potential window also remained constant at 1.65 V, but the potential showed a slight increase to values between 2.32 V and 3.97 V vs. Li/Li\(^+\). The rise in the potential of the graphite electrode could be caused by a lowering of the SOC of the electrode, which would indicate a loss of some of the preloaded lithium ions from the graphite structure. In spite of the 130 mV safety window, the graphite electrode potential was slightly negative during the charging step, which implies a possibility of lithium plating on the graphite surface. However, the decrease of the specific energy during cycling was very small, which suggested that the loss of cyclable lithium was not significant. Moreover, during the disassembling of the cells after the measurements, no signs of metallic lithium deposits were observed on the surface of the graphite electrode. Thus, it is likely that the very slightly negative graphite electrode potential observed during the charging of the LIC could be caused by the \(iR\)-voltage loss of the thick 1.55 mm separator used in the tests.
Fig. 4. The cycling stability of the prelithiated graphite/CDC LIC during 1000 cycles at a current density of 2 mA cm$^{-2}$ in a voltage window of 2.0–4.0 V. (a) The specific energy and the energy efficiency as a function of the cycle number; (b, c) the potentials of the positive and negative electrodes measured against a Li/Li$^+$ reference and the cell voltage during the 1$^{\text{st}}$ cycle (b) and the 1000$^{\text{th}}$ cycle (c).

When the shapes of the potential profiles in Figs. 4b and 4c are studied more closely, it can be seen that the slope of the CDC potential curve is slightly different above 3.0 V vs. Li/Li$^+$ compared to the slope below 3.0 V vs. Li/Li$^+$. At the higher potentials, the sloping of the profile is more subtle,
corresponding to a higher capacitance, compared to the slope at lower potentials. During the cycling of the graphite/CDC LIC between 2.0 V and 4.0 V, different processes occur on the CDC positive electrode in the lower end of the cell voltage window when compared to the higher end, causing the observed difference in the capacitance of the CDC material. Above the immersion potential of CDC (at LIC cell voltages of 3.0–4.0 V) PF$_6^-$ anion adsorption/desorption occurs on the surface of CDC during charging/discharging, whereas below the immersion potential (at cell voltages of 2.0–3.0 V), lithium ion adsorption/desorption takes place. [19,21,46] Similar behavior was also seen for the activated carbon electrodes in the LiPF$_6$ electrolyte in the CV in Fig. 1.

3.3 LIC with prelithiated LTO as the negative electrode

To overcome the problems of the high polarization of the graphite electrode and the possible lithium plating, LICs with LTO as the negative electrode were investigated as well. Nanosized LTO is known for its good power performance and long cycle life and is therefore an excellent candidate for the negative electrode of a LIC [8,15,47]. The potential profile of the LTO electrode as a function of the SOC is shown in Fig. 5. As can be seen from the figure, the potential of the LTO electrode remains nearly constant at around 1.55 V vs. Li/Li$^+$ almost over the entire SOC range. A sloping potential behavior is seen only at SOCs near 0 % and 100 %. This potential behavior is typical for LTO, and it is usually considered to result from a two-phase reaction mechanism between the Li$_4$Ti$_5$O$_{12}$ phase and lithiated Li$_7$Ti$_5$O$_{12}$ phase [18,48,49]. Compared to graphite (Fig. 2), LTO shows less polarization, which implies that the voltage losses of the LIC could be reduced when LTO is used as the negative electrode in the cell.
Fig. 5. The potential profile of the LTO electrode as a function of SOC during a charge-discharge cycle at 0.02C measured in the half-cell configuration. The SOC range of the LTO electrode utilized during the cycling of the prelithiated LTO/CDC LIC is also indicated in the figure. The LTO electrode was prelithiated to 50 % SOC.

In the first series of experiments with LTO/CDC cells, the LTO electrode was prelithiated to a SOC of 50 %. The charge balancing of the cell was chosen to be similar to the balancing of the graphite/CDC cell. Thus, the cell was assembled with a positive to negative electrode mass ratio of \( r = 0.9–1.0 \) \( (r = m_{\text{CDC, active}}/m_{\text{LTO, active}}) \). When the cell was cycled in a voltage window from 1.55 V to 2.55 V, the capacity of the CDC electrode corresponded to roughly 20 % of the theoretical capacity of the LTO electrode. Accordingly, the SOC range of the LTO electrode that was utilized during the cycling of the LIC was approximately at 50–70 % SOC (Fig. 5). In this range, the potential of the LTO electrode remains constant in the two-phase region plateau. A CV was also measured for the prelithiated LTO/CDC cell, and it confirmed the stable potential of the LTO electrode, since only capacitive response was observed (Fig. S2 in the Supplementary data). As in the case of the graphite/CDC cell, the cycling voltage range of the LTO/CDC cell could have been extended to the region where lithium ion adsorption/desorption occurs on the CDC positive electrode (i.e. at CDC potentials < 3 V vs. Li/Li\(^+\), corresponding to cell voltages < 1.55 V). However, the usable energy at cell voltages below 1.55 V is very low and thus the lower range of the CDC potential window was not utilized in the LTO/CDC LIC.

Fig. 6a presents the cycling stability of the LTO/CDC LIC measured in a three-electrode cell at a current density of 2 mA cm\(^{-2}\) in the voltage window from 1.55 V to 2.55 V. The cell stability was good; the energy retention after 1000 charge-discharge cycles was 97.5 %. Moreover, the
coulombic efficiency remained at a minimum of 99.8 % throughout the cycling, being slightly lower during the first few cycles and then remaining at values above 99.9 % through the rest of the cycles. A specific energy of 26.2 Wh kg⁻¹ was obtained at 2 mA cm⁻², and the energy efficiency was above 94.0 %.

The potential profiles of the positive and negative electrodes together with the cell voltage during the 1st and the 1000th cycle are presented in Figs. 6b and 6c. During the 1st charge-discharge cycle, the LTO potential swung in a window of 0.09 V from 1.51 V to 1.60 V vs. Li/Li⁺, and the CDC potential swing was 0.91 V between the values of 3.15 V and 4.06 V vs. Li/Li⁺. Compared to the potential swing of the graphite negative electrode (0.35 V) in Section 3.2, the potential variation of the LTO electrode during cycling at 2 mA cm⁻² was lower. Accordingly, when LTO was used as the negative electrode of the LIC, the capacity of the CDC could be utilized better in the studied voltage window. (Note, however, that the chosen cell voltage window was narrower for the LTO/CDC cell compared to the graphite/CDC cell.) During the 1000th cycle, the LTO potential window had slightly widened to 0.10 V, from 1.51 V to 1.61 V vs. Li/Li⁺, and the CDC potential window was correspondingly somewhat narrower, 0.90 V, in a window from 3.16 V to 4.05 V vs. Li/Li⁺. The widening of the LTO potential window could result from an increase in the resistance of the electrode. On the other hand, the average potential of the LTO electrode remained almost constant throughout the cycling, which indicates that the lithiation degree of the electrode remained in the two-phase region of LTO.
Fig. 6. The cycle life behavior of the prelithiated LTO/CDC cell during 1000 cycles at 2 mA cm$^{-2}$ in a voltage window of 1.55–2.55 V. (a) The specific energy and the energy efficiency as a function of the cycle number; (b, c) the potentials of the positive and negative electrodes measured against a Li/Li$^+$ reference and the cell voltage during the 1$^{st}$ cycle (b) and the 1000$^{th}$ cycle (c).

The specific energy of the LTO/CDC cell (26.2 Wh kg$^{-1}$) at a current density of 2 mA cm$^{-2}$ was rather low compared to that of the graphite/CDC cell (65.5 Wh kg$^{-1}$). The difference is mostly caused by the lower operating potential of the graphite electrode, leading to a higher cell voltage and a wider potential window utilizable at the positive electrode. However, the balancing of the
cells also has an effect. The capacity ratio of the CDC electrode to the LTO electrode was not optimized in the experiments described above but rather it was chosen to be comparable to the charge balancing of the graphite/CDC LIC. Furthermore, when the LTO electrode was prelithiated, it was necessary to oversize its capacity with respect to the capacity of the CDC electrode in order to accommodate the predoped lithium ions in the LTO structure and still provide enough capacity for charging the LIC. If the prelithiation step is omitted, the active material loading of the LTO electrode can be lowered, and thus a higher specific energy is expected. Therefore, a brief series of experiments was conducted in which the use of LTO as the negative electrode without prelithiation was examined.

3.4 LIC with non-prelithiated LTO as the negative electrode

The prelithiation of the negative electrode can be a time consuming process. It also introduces an additional manufacturing step to the production of LICs, which compromises the cost effectiveness from the industrial point of view. Moreover, metallic lithium is difficult and dangerous to handle in large amounts during mass production. Thus, being able to produce LICs without the need to prelithiate the negative electrode would be beneficial. According to Naoi et al. [16], the prelithiation of the LTO negative electrode is not necessary. Unlike with graphite, the consumption of lithium ions from the electrolyte is not a problem with LTO because it operates inside the electrolyte stability window. Moreover, as seen in Fig. 5, the LTO potential reaches the desired value of 1.55 V vs. Li/Li⁺ at a very low degree of lithiation, around 5 % SOC.

Thus, a brief series of measurements was made in which the prelithiation of the LTO electrode was omitted. This system was studied only in two-electrode configuration without a reference electrode. With this setup, a thinner separator (0.26 mm) can be used, and thus it presents a more realistic system to study the characteristics of the LIC in real-life use. As there was no need to accommodate the predoped lithium ions in the LTO structure, the thickness of the LTO electrode was made roughly 60 % thinner compared to the prelithiated LTO electrode. A non-prelithiated LTO/CDC cell (hereafter referred to as NPL-LTO/CDC cell) was prepared with a positive to negative electrode mass ratio of $r = 2.5$ ($r = m_{CDC,active}/m_{LTO,active}$). With this mass ratio, the capacity of the CDC electrode in the 1.0 V voltage window used for the LTO/CDC LIC corresponded to roughly 50 % of the theoretical capacity of the LTO electrode. As stated earlier, the lithium intercalation reaction at the LTO electrode is sluggish compared to the capacitive process at the CDC electrode. Therefore,
the power performance of the LIC could be compromised if the current density at the LTO electrode becomes very high. For this reason, the LTO electrode was still somewhat oversized in capacity compared to the CDC electrode in the experiments with the non-prelithiated LTO. [50]

Fig. 7a shows the cycling stability of the NPL-LTO/CDC cell measured in the two-electrode setup at a current density of 4 mA cm\(^{-2}\). The charge-discharge curves of the 1\(^{\text{st}}\) and the 1000\(^{\text{th}}\) cycle are presented in Figs. 7b and 7c, respectively. It is immediately seen from the charge-discharge curves in Figs. 7b and 7c that there is a deviation from a purely capacitive response at cell voltages below 1.9 V. From the half-cell experiments (Fig. 3) and the three-electrode measurements with the prelithiated LICs (Figs. 4 and 6), it is known that the potential response of the CDC electrode is linear as a function of SOC. Therefore, the curving of the cell voltage response must arise from the non-prelithiated LTO electrode. The curving of the cell voltage profile is caused by the changing potential of the LTO electrode in the cell voltage range below 1.9 V. The LTO electrode was not prelithiated to a SOC in the two-phase region experiencing a potential plateau at 1.55 V vs. Li/Li\(^+\). Thus, the potential of the LTO electrode changes until the cell is charged to a voltage where the lithiation degree of LTO corresponds to a SOC above approximately 5 % (see Fig. 5). A CV of the NPL-LTO/CDC cell is shown in Fig. S3 in the Supplementary data where the same behavior can be seen.

Because the capacity delivered by the cell was very low at voltages below 1.7 V, the lower cut-off limit of the cell voltage was raised to 1.65 V. In the voltage window of 1.65–2.55 V and a current density of 4 mA cm\(^{-2}\), the NPL-LTO/CDC cell showed a specific energy of 28.5 Wh kg\(^{-1}\) and the energy efficiency was over 92.3 % (Fig. 7a). Due to the changing potential of the LTO electrode, which operates partly in the single-phase region, the lower cell cut-off voltage is reached before the full capacity of the CDC electrode is utilized. Thus, the capacity of the LIC is reduced compared to the prelithiated LTO/CDC cell. Therefore, the obtained specific energy of the NPL-LTO/CDC cell was not as high as expected based on the results from the tests with the prelithiated LTO/CDC cell.
Fig. 7. The cycle life behavior of the NPL-LTO/CDC cell at a current density of 4 mA cm$^{-2}$ in a voltage window of 1.65–2.55V. (a) The specific energy and energy efficiency as a function of the cycle number; (b, c) the cell voltage profile during the 1$^{st}$ galvanostatic charge-discharge cycle (b) and the 1000$^{th}$ cycle (c).

The energy retention after 1000 charge-discharge cycles was 92.2 % and the coulombic efficiency remained at a minimum of 99.8 % throughout the cycling. It is noted that omitting the prelithiation step also has an effect on the cycle life stability of the NPL-LTO/CDC cell. As there is no excess lithium, even small changes in the amount of electrochemically active lithium in the cell affect the
performance. In the prelithiated LTO/CDC cell, there is a reserve of active lithium, and thus the effects of any lithium-consuming side reactions are not detected as clearly during cycling. Even if active lithium is lost, the potential of the LTO electrode will remain constant until the SOC decreases to values corresponding to the single-phase region of LTO (below 5 % SOC). However, when comparing Figs. 4 and 6 to Fig. 7, it should also be noted that the separator in the NPL-LTO/CDC cell was thinner, and thus the cell contained a smaller amount of electrolyte.

3.5 Comparison of the different LIC cell types

In order to be able to investigate the characteristics of the LICs in a more realistic system, the prelithiated LICs were also studied in the two-electrode setup with a thinner (0.26 mm) glass fiber separator. Moreover, this made the comparison of the prelithiated chemistries to the non-prelithiated one easier. The specific energies obtained in the two-electrode setup for the different cell types at current densities ranging from 0.4 mA cm$^{-2}$ to 4 mA cm$^{-2}$ are presented in Fig. 8a. The specific capacitances calculated for the CDC in the cells are presented in Fig. 8b.

The graphite/CDC cell gave the highest specific energy, delivering a maximum of 89 Wh kg$^{-1}$ on an active material basis. This value is in line with those reported earlier for LICs using carbonaceous negative electrodes; other authors have reported specific energy values ranging from 82 Wh kg$^{-1}$ to 104 Wh kg$^{-1}$ [20–22,25,28–30]. Both of the LTO cell chemistries gave similar specific energies; the prelithiated LTO/CDC cell delivered 30 Wh kg$^{-1}$ and the NPL-LTO/CDC cell 33 Wh kg$^{-1}$. These values are similar to those reported by Cericola et al. [14] for a LTO/activated carbon LIC (30 Wh kg$^{-1}$). However, other authors have reported specific energy values as high as 69 Wh kg$^{-1}$ for optimized LTO/activated carbon LICs [17] and 41–45 Wh kg$^{-1}$ when using graphene-based materials as the positive electrode instead of activated carbon [33,36].
Fig. 8. A comparison of (a) the specific energies and (b) the specific capacitances of CDC obtained at different current densities for the three LIC cell types. The applied cell voltage limits were 2.0–4.0 V for the graphite/CDC cell, 1.55–2.55 V for the prelithiated LTO/CDC cell and 1.65–2.55 V for the NPL-LTO/CDC cell. The specific capacitances were calculated in the voltage range from 0.95\(U_{\text{max}}\) to 0.8\(U_{\text{max}}\).

Although the specific energy of the graphite/CDC LIC was higher compared to the LTO/CDC cells, it decreased more pronouncedly when the current density was increased. Indeed, the \(iR\)-voltage loss, determined from the recovery of the cell voltage at the interruption of the discharge current, was higher in the cell with the graphite negative electrode compared to the LTO based cells. The \(iR\)-voltage loss of the graphite/CDC cell was around 170 mV at a current density of 4 mA cm\(^{-2}\), whereas for the prelithiated LTO/CDC cell the corresponding value was 60 mV, and for the NPL-LTO/CDC cell it was 80 mV. The difference in the cell voltage losses is considered to arise from the greater polarization of the graphite negative electrode compared to LTO, as seen also in Figs. 3 and 5.
Similar specific capacitance values of approximately 120 F g⁻¹ were obtained for the CDC in all of the LICs with different negative electrodes when a low current density of 0.4 mA cm⁻² was used (Fig. 8b). However, there were differences between the cell types in how well the capacitance of the CDC could be utilized during the cycling of the LICs especially at higher currents. The most efficient use of the CDC capacitance was obtained with the prelithiated LTO/CDC cell. This is explained by the extremely constant potential of the prelithiated LTO during the cycling of the LIC as well as the lower cell polarization, leading to a relatively wider potential window on the CDC positive electrode. It should be noted, however, that the voltage window of the LTO/CDC cell was narrower compared to the graphite/CDC cell. With the graphite/CDC cell, although a wider cell voltage window could be applied, the polarization of the negative electrode was higher, leading to a narrowing of the CDC potential range. This is seen as a lower CDC specific capacitance especially at higher currents. In the case of the NPL-LTO/CDC cell, in turn, the curving of the LTO potential profile at low SOCs causes a high potential swing on the negative electrode which narrows the potential window at the CDC electrode. Thus, the gain in specific energy due to the lower active material mass compared to the prelithiated LTO/CDC cell is modest. All in all, although omitting the prelithiation step is desirable from the manufacturing perspective, prelithiation does offer a noteworthy improvement in the electrochemical properties of the LTO/CDC cell. By preparing a prelithiated LTO/CDC LIC with a lower degree of prelithiation and a lower excess of LTO (in this study, the capacity of the CDC electrode corresponded to 20 % of the capacity of the prelithiated LTO electrode), the specific energy of the LTO/CDC cell could be improved.

The specific capacitance obtained for the CDC in this study, 120 F g⁻¹, is appreciable, yet similar to the values reported for other carbon materials as well. The specific capacitance values of activated carbon in lithium-containing electrolytes reported by other authors range from 60 to 165 F g⁻¹ [8,17,21,22,28,39]. For example, Krause et al. [39] obtained a specific capacitance of approximately 110 F g⁻¹ for their carbon black electrodes in a LIC with a LiFePO₄ positive electrode. (In their study, the capacitive electrode was the negative electrode.) On the other hand, much higher specific capacitance values have also been reported, for example, by Stoller et al. [33]. They reported a specific capacitance of 266 F g⁻¹ for chemically activated graphene in a LIC using graphite as the negative electrode. However, in their publication, long term cycling data was not provided to estimate the stability of the cells. [33] All in all, the performance of the CDC in the LICs in this study was promising; a stable performance was demonstrated and a good specific capacitance was obtained for the CDC material. Moreover, we believe that further improvement could be achieved by optimizing e.g. the balancing of the cells [50], the electrolyte properties [35]
and the porosity of the CDC [7]. The uniqueness of CDC materials is the narrow pore size distribution, which can be carefully controlled during the carbon manufacturing process. Thus, it could be possible to still improve the CDC performance by tailoring its properties to better match the lithium-containing electrolyte.

4. Conclusions

In this work, the use of CDC as the positive electrode material for LICs was investigated by assembling cells utilizing two different negative electrode materials, LTO and graphite. The graphite electrodes were prelithiated before assembling the LICs, and LTO containing cells were studied with and without prelithiation. A specific energy of roughly 90 Wh kg\(^{-1}\) on an active material basis was obtained for the graphite/CDC cell, when the cell was cycled in a voltage range from 2.0 V to 4.0 V. Both of the LTO based cell chemistries gave similar specific energies of around 30 Wh kg\(^{-1}\). The prelithiated LTO/CDC cell was cycled in a voltage window from 1.55 V to 2.55 V, and the non-prelithiated LTO/CDC cell was cycled in a slightly narrower voltage window between 1.65 V and 2.55 V. The graphite/CDC LIC delivered the highest specific energy due to the low operating potential of the graphite negative electrode which enables a high cell voltage and the utilization of a wide potential range at the CDC positive electrode. On the other hand, the polarization of the graphite electrode during cycling was observed to be higher compared to LTO leading to higher voltage losses. Consequently, the CDC potential window is narrowed and the CDC capacity decreased at high currents. Prelithiated LTO provided the most stable negative electrode potential and the lowest voltage losses of the studied negative electrodes, thus enabling a more efficient utilization of the capacitance of the CDC electrode. However, the usable cell voltage window was narrower with LTO negative electrode when compared to graphite.

LTO offers a further advantage of being able to operate as the negative electrode of a LIC without predoping with lithium ions. Prelithiation adds another step to the manufacturing process of LICs and therefore increases the cost. When the prelithiation of the LTO electrode was omitted, the active material loading of the electrode could be decreased, which led to an expected increase in the specific energy of the cell. However, omitting the prelithiation caused the LTO electrode to operate partly outside of the two-phase region, where the potential of LTO is not constant during the
cycling of the LIC. Accordingly, the potential range of the CDC electrode utilized during the cycling of the LIC was reduced, and the gain in specific energy was not as high as expected based on the decrease in active material mass.

The nanoporous CDC appeared as a promising candidate for the use as the positive electrode in LICs. It showed a good performance with all of the studied negative electrode materials; a specific capacitance of 120 F g$^{-1}$ in the lithium-containing electrolyte was demonstrated with good stability over 1000 charge-discharge cycles. Moreover, we believe that the performance of the systems studied here could be improved by optimizing the mass balancing of the electrodes as well as the electrolyte properties, such as salt concentration and the solvent. Also, the porosity of the CDC material could possibly be optimized further, as one of the advantages of CDC as an electrode material is its narrow pore size distribution which can be accurately controlled during the manufacturing process.

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