

1 **High-Capacity Reversible Lithium Storage in Defined Microporous Carbon** 2 **Framework for All Solid-State Lithium Batteries**

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7 8 9 **Abstract**

10 For decades graphite has been used as the anode material of choice for lithium batteries since porous
11 carbons were believed to be inappropriate because of their high potential slope during lithiation as well
12 as capacity losses due to intense formation of solid electrolyte interphase (SEI).

13 However, in this work we demonstrate a microporous carbide-derived carbon material (HCmicro) to
14 provide a high-capacity anode framework for lithium storage in all solid-state batteries. Half-cell
15 measurements of HCmicro exhibit exceptionally high and reversible lithiation capacities of
16 1000 mAh g⁻¹_{carbon} utilizing an extremely long voltage plateau near 0 V vs. Li/Li⁺. The defined
17 microporosity of the HCmicro combined well with the argyrodite-type electrolyte (Li₆PS₅Cl)
18 suppressing extensive SEI formation to deliver high coulombic efficiencies. Preliminary full-cell
19 measurements vs. NMC-cathodes (LiNi_{0.9}Co_{0.05}Mn_{0.05}O₂) obtained a considerably improved average
20 potential of 3.76 V leading to a projected energy density as high as 443 Wh kg⁻¹. ⁷Li Nuclear Magnetic
21 Resonance spectroscopy was combined with ex-situ Small Angle X-ray Scattering and further
22 electrochemical investigations to elucidate the storage mechanism of lithium inside the carbon matrix
23 revealing the formation of extended quasi-metallic lithium clusters.

24 25 **Introduction**

26 The development of batteries for consumer electronics continually advances volumetric and gravimetric
27 energy density leading to smaller and lighter devices. For electric vehicles, longer range and higher
28 energy density are desired. Lithium metal anodes are attractive candidates to fulfil these goals, owing to
29 their high theoretical specific capacity of 3860 mAh g⁻¹ and low voltage of -3.04 V vs. SHE. However,
30 due to the high reactivity of lithium metal causing dendrite formation and electrolyte decomposition,
31 long-term cycling remains problematic under practical conditions.¹⁻⁴ Stable negative electrodes like
32 commercial graphite, on the other hand, suffer from low theoretical specific capacity with only little
33 opportunity for further optimization. The ideal anode material therefore combines the high gravimetric
34 capacity of a lithium metal anode with the cycle stability of a graphite anode, gaining long-life batteries
35 with high energy density.

1 Over the last decades, progress has been made in increasing the lithiation capacity of carbon materials.
2 Several hard carbons (HC) or micro- and mesoporous carbons have been presented exceeding the
3 theoretical capacity of graphite of 372 mAh g^{-1} . Some of them show high specific capacities of
4 1500 mAh g^{-1} or even beyond in the 1st lithiation.⁵⁻⁸ However, most of them suffer from limited
5 reversible capacity and usually exhibit a very long so-called sloping region in their voltage profiles,
6 which considerably lowers the resulting full-cell voltage.

7 Increasing anode capacity at a lower voltage plateau requires the formation of metallic lithium though,
8 which needs to be stabilized for reversible cycling. By adapting the liquid electrolyte and additives or
9 by applying pressure, the long-term stability of lithium-metal batteries could be increased as just recently
10 reported by Dahn et al.^{9,10} However, especially at room temperature, plating and stripping of lithium is
11 limited to certain current densities and capacities.¹¹ When leaving the narrow range of suitable
12 parameters, dendrite formation and porous lithium growth occur as reviewed e.g. by Zhang et al.^{4,12} By
13 directing lithium deposition, e.g., using a porous host matrix, a defined interface can be formed that
14 inhibits side reactions with the electrolyte and the effective current density is reduced leading to an
15 enhanced cycle life.¹³⁻¹⁷

16 A porous carbon material is a good choice as anode material due to its low weight, tunable pore
17 architecture and good electric conductivity. The microporous structure is able to stabilize molecules or
18 metal clusters by decreasing their chemical potential.¹⁸⁻²⁰ Hence, pores potentially act as seeding sites
19 directing lithium deposition preferentially towards the pore interior. The formation of lithium quasi-
20 metallic clusters – microscopic aggregates consisting of a few tens through a few hundreds of lithium
21 atoms²¹ – in the inner porosity of HCs was detected by Tatsumi et al. by ^7Li nuclear magnetic resonance
22 (NMR) measurements.²² Cluster formation is one possibility to store excess lithium at low potentials vs.
23 Li/Li^+ . Only recently, an operando ^7Li NMR study on HC and graphite half-cells has been published by
24 Gotoh et al. investigating overlithiation behavior of the lithium NMR signal in different carbon
25 materials.²³

26 We envisioned carbide-derived carbons (CDCs) to offer an ideal microporous carbon framework for
27 stabilizing lithium clusters due to their narrow pore size distribution, which can be precisely tuned.²⁴⁻²⁷
28 However, their high porosity comprises pores that are accessible for small molecules like N_2 or liquid
29 electrolyte components as well as defect sites in the hexagonal carbon structure. In combination with
30 the electronic conductivity of the carbon, both tend to deplete liquid electrolytes and promote solid
31 electrolyte interphase (SEI) formation leading to irreversible lithium and capacity losses.^{8,15}

32

33 In the following we demonstrate the application of a defined microporous carbide-derived carbon
34 (TiC-CDC ,²⁸ further named as HCmicro) as a carbon/lithium hybrid anode within an all solid-state
35 battery (ASSB) set-up that tackles these challenges and reveals clear advantage compared with a
36 commercial hard carbon (HC). Unlike solvent-based electrolytes, the solid electrolyte cannot penetrate
37 the accessible porosity of the framework, which is why this system suppresses extensive SEI formation

1 on accessible micropores, and thus, leads to reduced capacity loss in the first cycles as well as long-term
2 stabilization of lithium deposited inside the pores. Half-cell measurements of HCmicro exhibit
3 exceptionally high and reversible lithiation capacities of up to 1000 mAh g⁻¹_{carbon} utilizing an extremely
4 long voltage plateau region near 0 V vs. Li/Li⁺. Even at room temperature, no short circuit due to
5 dendrite formation is observed. With the solid electrolyte the herein presented system comprises a
6 remarkably high coulombic efficiency (CE) of 70% in the 1st cycle in comparison with other battery
7 systems utilizing accessible microporous carbon materials, which usually have an initial CE in the range
8 of 30 to 50%.^{5,6} Via magic angle spinning (MAS) ⁷Li NMR measurements we demonstrate the lithiation
9 mechanism to rely on lithium cluster formation inside the pores with special features for the HCmicro-
10 electrode. The latter, to the best of our knowledge have not been observed for lithiated carbon electrodes
11 so far.^{22,23,29–34} Based on these findings, we propose a lithiation mechanism of HCmicro in the all solid-
12 state system via the reversible formation of extended lithium clusters in the carbon framework.

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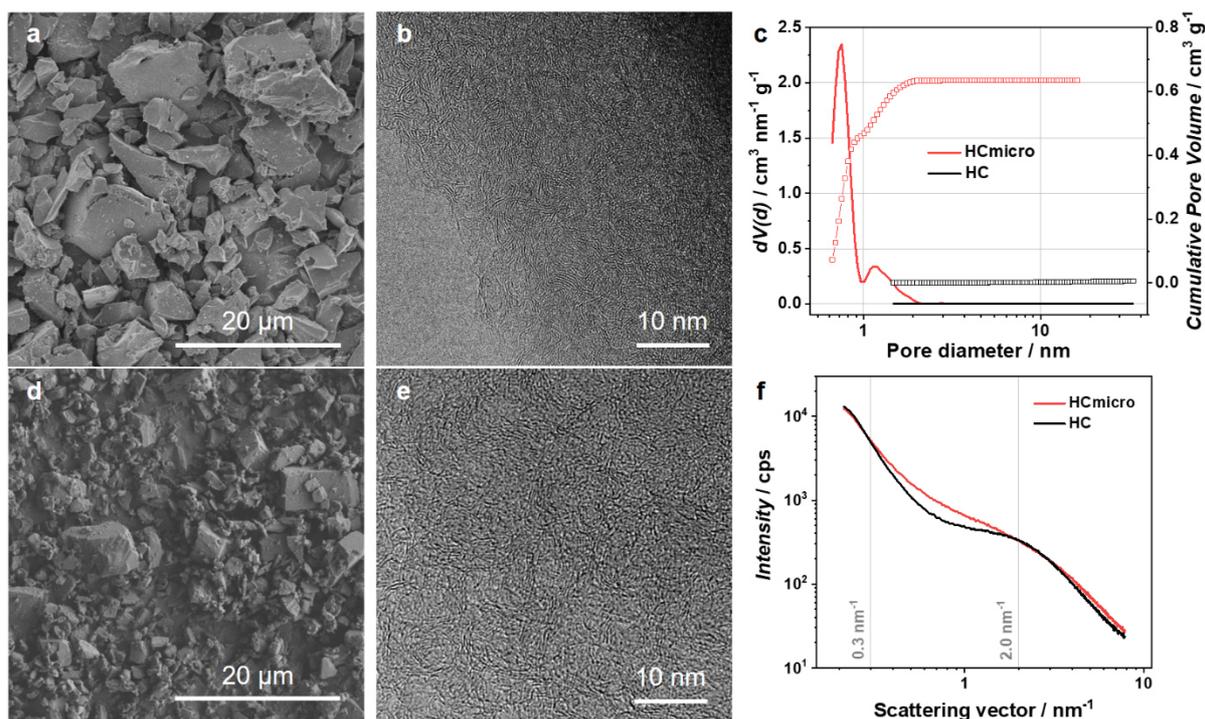
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15 **Structural and morphological characteristics of the porous carbon structure**

16 The microporous carbon HCmicro and the commercial HC chosen as reference were initially
17 investigated with regard to their structural and morphological features (Figure 1). Scanning electron
18 microscopy (SEM) and transmission electron microscopy (TEM) revealed the differences of both
19 carbons in terms of carbon nanostructure and particle size. SEM images display particle diameters of
20 around 10 μm for the HC compared to 5 μm for HCmicro while both samples also contain much smaller
21 particles in the range of 1 μm and below. Both carbons show irregular shaped particles with sharp edges.
22 The TEM images depict differences in size and shape of graphite-like domains between HCmicro and
23 HC. These domains show random turbostratic orientation for both carbons with shortened average lateral
24 length of the parallel graphite-like segments for the HCmicro as well as decreased average curvature
25 radius in comparison with the HC. HCmicro additionally comprises a lower average number of parallel
26 stacked graphene sheets overall showing good agreement with literature results for both carbon
27 materials.^{35,36}

28 Nitrogen physisorption analysis at 77 K results in a type I isotherm for HCmicro (Supplementary
29 Figure 1) typical for microporous materials but no accessible porosity for the HC with a type II isotherm
30 characteristic for non-porous materials (according to the IUPAC classification³⁷). The specific BET
31 surface area and total pore volume are 1520 m² g⁻¹ and 0.63 cm³ g⁻¹ for HCmicro and 3.8 m² g⁻¹ and
32 0.006 cm³ g⁻¹ for HC, respectively. The pore size distributions of both carbons were determined via
33 quenched-solid density functional theory (QSDFT) calculations (Figure 1c). The main pore diameter in
34 HCmicro is 0.75 nm with 75% of its total pore volume reached at diameters up to 1 nm. Larger micro-
35 and small mesopores until the diameter of 3 nm contribute further. The HC, in comparison, comprises
36 nearly no accessible porosity for N₂ molecules resulting in a very low cumulative pore volume.

1 As established hard carbons are known to have closed intrinsic porosity, which means pore volume that
 2 is present within the material but remains inaccessible in gas physisorption for nitrogen as the probe gas
 3 at 77 K. Therefore, we measured Small Angle X-ray Scattering (SAXS) (Figure 1f) to investigate further
 4 the porosity of both materials.³⁸ Both SAXS measurements exhibit scattering curves with comparable
 5 intensities at scattering vectors (Q) above 2 nm^{-1} and below 0.3 nm^{-1} . The respective regions are mainly
 6 influenced by the scattering of the macroscopic particle surface area for small values of Q and the
 7 scattering on micropores for high Q values.³⁹ In the scattering region between 2 nm^{-1} and 0.3 nm^{-1} , a
 8 flattened sloping with higher scattering intensity is observed for HCmicro. According to Saurel et al.
 9 pore-pore connections occurring from fractal aggregates of pores lead to an increased contribution of
 10 the scattering between Q values corresponding to micropore and particle scattering.³⁹ This is due to the
 11 dimension of the fractal pore-pore connections. Such aggregates can be attributed to an accessible pore
 12 structure such as of HCmicro resulting in a higher scattering intensity and flattened slope in this region
 13 as observed in the SAXS curves. However, both curves show comparable intensities above 2 nm^{-1}
 14 revealing the existence of microporosity for both carbons that differs mainly in inter-pore connectivity.
 15
 16



17
 18 **Figure 1: Characterization of the carbon materials.** SEM and TEM images of HC (a and b,
 19 respectively) and HCmicro (d and e, respectively). Pore size distribution and cumulative pore volume
 20 (c) obtained from N_2 physisorption measurements at 77 K (Supplementary Figure 1) and SAXS data (f)
 21 for both carbons (red: HCmicro; black: HC).

22
 23 Further investigations via powder X-Ray Diffraction (PXRD) and Raman measurements are visualized
 24 and discussed in the supplementary material (Supplementary Figure 1). In summary, the materials are
 25 of comparable morphology and structure with probably slightly lower amount and size of graphite-like

1 domains for HCmicro. Both carbons possess porosity predominantly in the microporous range, however,
2 with different pore accessibility for N₂ molecules. This leads to the differentiation into “open porous
3 system” for the HCmicro and “closed porous system” for the HC.

6 **Calculation of maximum lithiation capacity for HCmicro**

7 Aurbach et al. proposed a possible lithiation capacity of 1400 mAh g⁻¹ for an activated microporous
8 carbon protected against electrolyte penetration by a pyrolytic carbon layer. They calculated the
9 theoretical maximum lithiation capacity based on the complete filling of the microporosity with lithium
10 metal. Practically, however, they have been able to gain only about 10% of this value due to incomplete
11 pore coverage leading to continuous SEI formation during lithium deposition.¹⁵ Our approach therefore
12 employs a solid electrolyte to avoid pore penetration by liquid and supersede any additional carbon
13 coverage e.g. to minimize weight of inactive material.

14 For calculation of the theoretical maximum of lithium-storage capacity of the herein used HCmicro, we
15 assumed the accessible total pore volume obtained from N₂-physisorption (0.63 cm³ g⁻¹_{HCmicro}) as
16 accessible void for lithium insertion.¹⁵ Assuming that the density of lithium stored in pores is similar to
17 the bulk density of lithium (0.534 g_{Li} cm⁻³), we can estimate the amount of storable lithium in the open
18 pore structure of HCmicro (0.336 g_{Li} g⁻¹_{HCmicro} or 1300 mAh g⁻¹). Compared to reversible lithiation
19 capacities of different HCs with a maximum of 550 mAh g⁻¹_{HC} in liquid electrolytes⁷ this corresponds
20 to an almost two and a half times higher reversible capacity.

21 For the definition of the testing parameters, irreversible capacity resulting from side reactions and an
22 incomplete pore filling due to geometric restrictions need to be considered. Hence, for the test protocol
23 in this work, a constant lithiation capacity of 1000 mAh g⁻¹_{carbon} was applied to compare the HCmicro
24 with the commercial HC.

27 **Electrochemical evaluation in half-cells vs. lithium metal**

28 For electrochemical evaluation of the materials in ASSBs, the carbons were prepared as powder
29 electrodes via blending the carbon with solid electrolyte (SE) and a conducting additive in a weight ratio
30 of 60:35:5. The resulting batch powders are denoted as “*active material-electrode*” (graphite-electrode,
31 HC-electrode and HCmicro-electrode) to differentiate from the pure carbon powder. Firstly, the
32 HCmicro-electrode and HC-electrode were evaluated against lithium metal foil. The resulting
33 electrochemical cell is named a “half-cell” due to evaluation of only one electrode (in this case the
34 carbon anode) of the intended battery cell that is then called a “full-cell”. All stated potential values in
35 this section are therefore measured vs. Li/Li⁺ and shall be read as V or mV “vs. Li/Li⁺” though this
36 phrase is not especially written for each individual case. The half-cells were electrochemically evaluated
37 in 10 cycles of lithiation of the carbon anode by discharging with 0.05 mA cm⁻² up to 1000 mAh g⁻¹_{carbon}

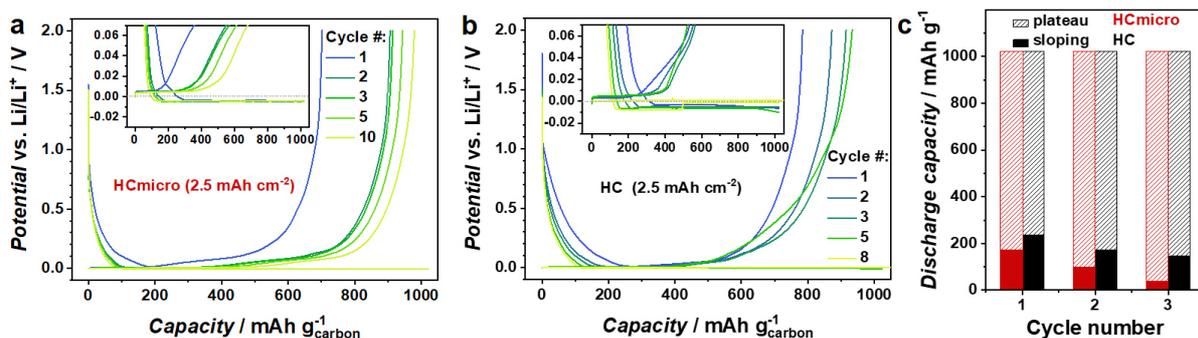
1 and subsequent charging/delithiation at the same current density until the voltage limit of 2 V was
2 reached (Figure 2).

3 The resulting voltage profiles for the lithiation of the HCmicro-electrode (Figure 2a) show a short and
4 steep voltage decrease followed by a long plateau below 20 mV. This plateau starts at 172 mAh g⁻¹_{HCmicro}
5 in the 1st cycle and stays above -5.5 mV until the end of lithiation at 1000 mAh g⁻¹ for all 10 cycles (see
6 inset). It is noteworthy that the voltage profiles do not comprise a nucleation dip at the beginning of the
7 plateau region. This temporary decrease in cell potential is associated with overcoming the overpotential
8 for the nucleation of lithium metal on a substrates surface and is therefore assigned to the start of lithium
9 metal plating.²³ The delithiation of the HCmicro-electrode exhibits a very long plateau region close to
10 0 V divided into two parts before the voltage increases sharply at the end of delithiation. During the first
11 delithiation, the first plateau (up to 20 mV) contributes to 210 mAh g⁻¹_{HCmicro} and the second plateau
12 (above 20 mV) adds another 332 mAh g⁻¹_{HCmicro} until the voltage reaches 0.2 V. In total, the plateau
13 capacity reaches 542 mAh g⁻¹_{HCmicro} in the 1st and 827 mAh g⁻¹_{HCmicro} in the 10th cycle. Generally, minor
14 capacity values are obtained in the sloping region above 0.2 V, i.a. due to the nature of the solid
15 electrolyte not being able to form an electrochemical double layer.

16 The HC-electrode half-cell (Figure 2b) shows a different behaviour in the 1st cycle. The discharge
17 voltage curve falls below -5.5 mV after a capacity of 880 mAh g⁻¹_{HC} and continues to decrease. In further
18 discharge cycles, the cell voltage crosses -5.5 mV shortly after the end of the sloping region forming a
19 slight dip. In the 8th cycle, the voltage signal experiences a sharp rise to 0 V after merely 495 mAh g⁻¹_{HC}
20 of lithiation indicating the formation of a dendrite. Consequently, the cell cannot reach the upper cut-off
21 voltage in the subsequent charging step. However, the 1st charging profile of the HC half-cell still shows
22 a plateau capacity of 338 mAh g⁻¹_{HC} up to 20 mV, corresponding to an increase of ca. 60% when
23 compared to the HCmicro-electrode. The second plateau until 0.2 V exhibits a capacity of
24 282 mAh g⁻¹_{HC} and is therefore shortened in comparison to the HCmicro-electrode (total plateau
25 capacity of 620 mAh g⁻¹_{HC}).

26 The two plateaus formed in delithiation of the carbons indicate the existence of two different delithiation
27 mechanisms occurring in both carbons to different extent. The plateau up to 20 mV can be attributed to
28 the stripping of metallic lithium from a 3D structured conducting material due to the small hysteresis
29 between plating and stripping in the case of low current densities (0.05 mA cm⁻²).⁴⁰ The other
30 delithiation plateau between 20 mV and 0.2 V cannot be assigned to a certain species at this point.

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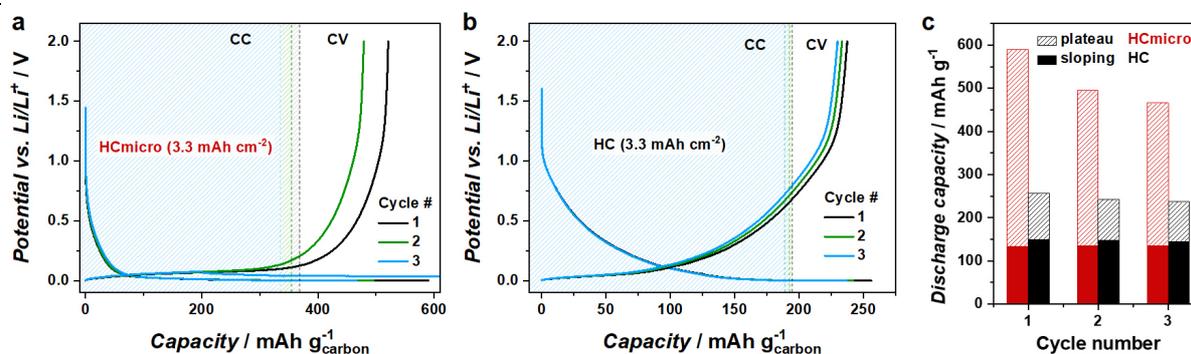
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 2 **Figure 2: Electrochemical characterization via constant current (CC) measurement.** Voltage
 3 profiles of HCmicro (a) and HC (b) half-cells vs. lithium metal galvanostatically cycled at 0.05 mA cm⁻²
 4 between 2 V and a constant capacity of 1000 mAh g⁻¹ carbon in discharge with an areal loading of
 5 2.5 mAh cm⁻². (c) Comparison of sloping (until 20 mV, filled area) and plateau discharge capacities
 6 (below 20 mV, hatched area) for both carbon half-cells in the first 3 cycles.

7
 8 The HCmicro half-cell reaches slightly lower initial CE (70%) than the HC half-cell (77%) but improves
 9 rapidly to 98% CE with a delithiation capacity of 980 mAh g⁻¹ HCmicro in the 10th cycle. In contrast, the
 10 HC half-cell fails in 8th lithiation due to micro short-circuit of the cell. The shown example for a HC
 11 half-cell, however, is no outlier. We tested various HC half-cells each failing due to short-circuit within
 12 their first 8 cycles while HCmicro half-cells did not show this phenomenon. Despite the fact that no
 13 liquid electrolyte penetrates the pores, the lower initial CE is not unusual for a porous carbon with a
 14 high specific surface area, since, e.g., lithium can react with carbon dangling bonds at the carbon surface.
 15 In the following cycles, the CE for HCmicro half-cell show remarkably high values compared to other
 16 carbon electrodes with N₂-accessible porosity stated in literature.^{5,6,41} The application of HCmicro in
 17 liquid electrolyte systems cannot compete with the herein stated all solid-state system in terms of CEs
 18 and delithiation capacities.^{8,28} This indicates that the combination of the open porous HCmicro with the
 19 solid electrolyte prevents penetration of electrolyte components into the microporous system and thus
 20 minimizes side reactions with lithium species located inside the carbon particle.

21
 22 As the constant current (CC) experiments exhibit a high capacity slightly below 0 V in the plateau
 23 region, we assumed a thermodynamically favoured formation of lithium species inside the carbon.
 24 Hence, we conducted a constant voltage measurement (ConVol) in which the half-cells were lithiated
 25 until 0 V, and subsequently a constant voltage of 0 V was applied until the current exceeds -7.5 μA cm⁻²
 26 (Figure 3). According to our understanding, bulk lithium metal should not deposit under these conditions
 27 since a certain overvoltage is normally required for plating. The resulting voltage profiles show a sloping
 28 region and continue with a plateau at the cut-off voltage of 0 V during discharge. The sloping and plateau
 29 capacities were separated at a potential of 20 mV to examine the differences between HC- and HCmicro-
 30 electrode (Figure 3c). The obtained capacities of the sloping region are quite comparable with slightly
 31 higher values close to 150 mAh g⁻¹ HC for the HC half-cell. However, the plateau capacities show a

1 remarkable difference with values of 108 to 92 mAh g⁻¹_{HC} for HC and 457 to 330 mAh g⁻¹_{HCmicro} for
 2 HCmicro half-cells. As the plateau capacity at 0 V in the delithiation of HCs was assigned to lithium
 3 insertion into microporous structure by Stevens and Dahn,⁴² we can presume that our measured capacity
 4 for the HCmicro-electrode results from lithium species forming inside the micropores. There are two
 5 possible lithium species known from literature forming at potentials near and slightly below 0 V –
 6 lithium clusters and lithium metal.^{23,31}
 7 For the interpretation of the ConVol measurements, it is important to state that the minimum potential
 8 of the cell in constant voltage step was at -0.5 mV slightly below the intended 0 V due to the precision
 9 of the measurement device. However, this is at least one order of magnitude smaller than the
 10 overpotential for lithium metal plating observed in CC experiments e.g. for Li-Ni-foil cell and Li-Li
 11 symmetric cell (Supplementary Figure 2). Therein the minimum of the potential dip attributed to the
 12 beginning of lithium metal plating was located at values of -64.0 mV and -5.0 mV, respectively.
 13 Additionally, the delithiation profile of the cells has only one plateau region at potentials between 0.02
 14 and 0.2 V corresponding to the higher potential plateau in CC measurements. The first plateau below
 15 0.02 V, previously assigned to the stripping of lithium metal, is missing. This suggests that no lithium
 16 metal plating occurs in these experiments. In contrast, it shows the high capacity-gain by another lithium
 17 form different from sloping capacity or formation of graphite intercalation compounds (GICs) like LiC₆
 18 (both above 0 V), and higher than cluster formation in hard carbons. In the 3rd charging cycle the
 19 HCmicro cell exhibits a short circuit due to dendrite formation caused by the lithium metal counter
 20 electrode. However, this has no influence on its previous performance and can be easily prevented by
 21 using less dendrite-prone counter electrodes than lithium metal, e.g., a lithium-indium alloy. The
 22 conducted cyclic voltammetry (CV) measurements on the HCmicro half-cell (see Supplementary
 23 Figure 3) confirm that no plating of lithium metal occurs at potentials above and at -5 mV as they do
 24 not comprise the classical plating/stripping peaks as visible in Li-Ni-foil cell cyclic voltammetry
 25 (Supplementary Figure 3) or shown by Bonino et al.⁴³

26
27



28
29 **Figure 3: Electrochemical characterization via constant voltage (ConVol) measurement.**
 30 Galvanostatic measurements including a constant voltage step at 0 V during discharge until a cut-off
 31 current of -7.5 μA cm⁻² for HCmicro (a) and HC (b) half-cells vs. lithium metal with constant current
 32 (CC, hatched area) and constant voltage (CV) regions of the discharge/lithiation voltage profiles

1 separated by dotted lines in (a) and (b). (c) The corresponding capacities for sloping (until 20 mV, filled
2 area) and plateau (below 20 mV, hatched area) region gathered from the discharge voltage profiles for
3 HC (black) and HCmicro (red).

4
5 In summary, the carbide derived carbon anode material (HCmicro) exhibits major advantages in half-
6 cell performance comprising plateau capacity near 0 V vs. Li/Li⁺, high CE and delithiation capacity.
7 HCmicro did not undergo any short-circuiting despite the fact that a high loading of 2.5 mAh cm⁻² was
8 cycled and the measurements were performed at room temperature. To fully understand and explain the
9 mechanism for this high plateau capacity, further investigations were conducted via NMR spectroscopy
10 and SAXS measurements.

11 12 13 **⁷Li NMR spectroscopy studies of lithiated electrode materials**

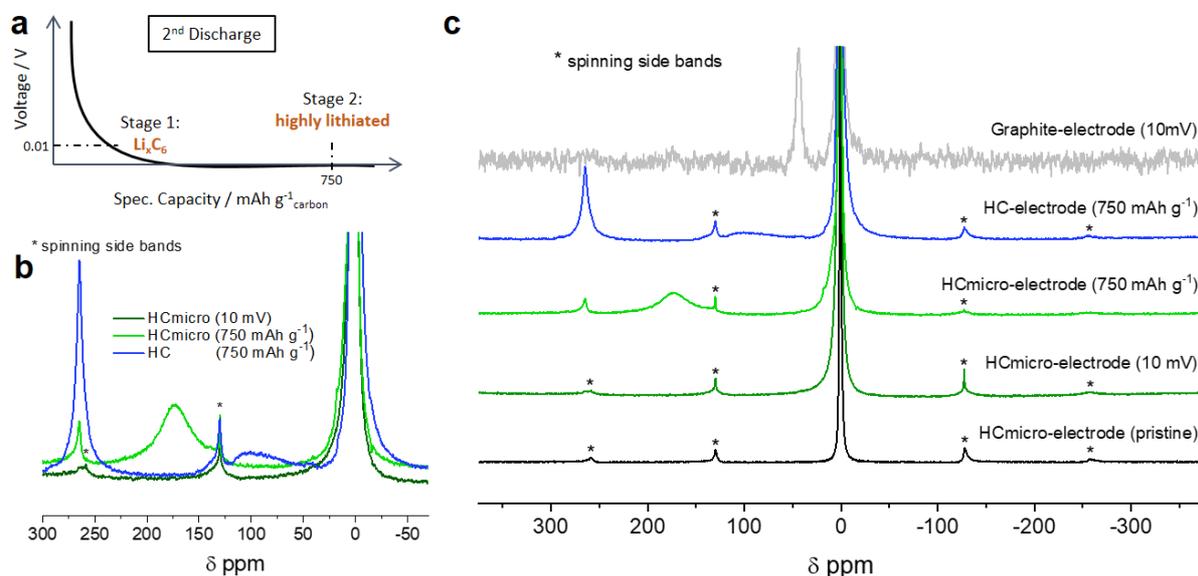
14 Magic angle spinning ⁷Li nuclear magnetic resonance (⁷Li MAS NMR) spectra were measured ex-situ
15 for varying stages of lithiation of graphite-, HC- and HCmicro-electrode to obtain further information
16 about the evolving lithium structures and lithiation mechanism in the described cell system (Figure 4).
17 Therefore, half-cells comprising the particular batch powders were pre-cycled once between 0.01 and
18 2 V and afterwards discharged (lithiation of active material) until a certain cut-off criterion. The chosen
19 cut-off criteria were defined as 10 mV (stage 1), the typical lithium intercalation cut-off for graphite
20 anodes, and 750 mAh g⁻¹_{carbon} (stage 2), for investigation of lithium species at highly lithiated stage
21 (Figure 4a). To investigate the influence of lithium contained in the SE, the NMR spectrum was also
22 measured on the pristine HCmicro-electrode. The resulting spectrum (Figure 4c) displays one intense
23 signal at 1 ppm with spinning side bands of first and second order marked with asterisks (*) in the
24 diagram. Signals with very low chemical shift against the reference LiCl arise from ionic lithium species.
25 Hence, the signal is attributed to lithium in the Li₆PS₅Cl argyrodite-type electrolyte.^{19,31}

26
27 The graphite-electrode material cycled to stage 1 (10 mV) was investigated to gain information about
28 the solid-state ⁷Li MAS NMR signal of intercalated lithium. In addition to the electrolyte signal at
29 1 ppm, the spectrum exhibits a peak at 48 ppm as expected from literature revealing full lithiation to the
30 graphite intercalation compound (GIC) stage I (LiC₆).⁴⁴⁻⁴⁶

31 The HCmicro-electrode lithiated until 10 mV did not develop any signal apart from the electrolyte
32 signal, which becomes slightly broadened compared with the pristine HCmicro-electrode. GICs with
33 lower lithium content like diluted stages III and IV⁴⁶ are located at low chemical shift in NMR and
34 therefore might overlap with the intense solid electrolyte peak at 1 ppm.^{45,47} The formation of GIC stage
35 I (LiC₆) in HCmicro is unlikely due to the low density of perfect graphitic domains observed in TEM
36 (see Figure 1). This explains the absence of the NMR peak at 48 ppm.

1 At 750 mAh g⁻¹_{HC} lithiation (stage 2) of the HC-electrode a very broad signal starting from
 2 approximately 35 ppm with its maximum at 105 ppm and almost reaching the first spinning side band
 3 of the electrolyte peak at 130 ppm occurs (Figure 4b and c). Besides the electrolyte peak also another
 4 signal at 263 ppm was observed. This signal can be assigned to metallic lithium deposited in the
 5 electrode powder according to literature.^{23,34,48} The broad signal around 105 ppm falls into the range
 6 between intercalation signals from 0-50 ppm and the lithium metal at 263 ppm. According to literature
 7 we therefore assign it to lithium clusters in the HC material.^{23,32,34,44,49}
 8 The HCmicro-electrode lithiated to stage 2 (750 mAh g⁻¹_{HCmicro}) exhibits a distinct broad signal centered
 9 at 175 ppm chemical shift. Further the signal at 263 ppm beforehand assigned to formation of lithium
 10 metal in the electrode powder occurs in addition to the electrolyte peak at 1 ppm. The metallic lithium
 11 signal is less intense for the HCmicro-electrode at stage 2 compared to the signal in the HC-electrode
 12 (Figure 4b). This hints to a smaller amount of lithium metal in the HCmicro-electrode as the integral in
 13 NMR corresponds to the number of associated nuclei at comparable sample weight. The short-circuit
 14 observed in electrochemical cycling of the HC half-cells in contrast to the HCmicro half-cells supports
 15 this observation (Figure 2b). The signal of the HCmicro-electrode at 175 ppm could not be assigned to
 16 any chemical shift in room temperature ⁷Li NMR spectra for disordered carbon electrodes known from
 17 literature.^{23,32,34,49} However, it also falls into the range of chemical shift predicted for lithium clusters
 18 between 50 and 263 ppm.⁴⁴

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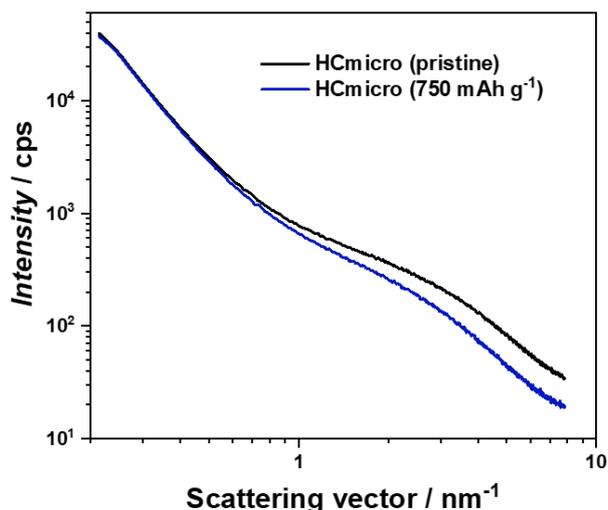
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 22 **Figure 4: ⁷Li NMR spectroscopy at different lithiation degree.** Schematic voltage profile of the half-
 23 cells in preparation for NMR measurement displaying second discharge with different cut-off stages for
 24 cell disassembly (a). Room-temperature ⁷Li MAS NMR spectra are shown with enlarged spectra of
 25 HCmicro-electrode at stages 1 and 2 and HC-electrode at stage 2 for detailed signal comparison (b). The
 26 full spectra of the different samples as described above are provided in (c). Spinning side bands are
 27 denoted by asterisks (*).

1
2 A number of research groups have studied lithium cluster formation in HCs in combination with liquid
3 electrolytes observing ^7Li NMR signals at chemical shifts between 50 ppm and 120 ppm at room
4 temperature.^{23,32,34,49} The relatively high chemical shift of 175 ppm observed for the lithiated HCmicro-
5 electrode is therefore rather unusual compared to literature-known HC cluster-signals and the herein
6 described HC-electrode measurements. There are two different possibilities to explain the observed
7 phenomenon. The first one is a higher free electron content in the clusters, which results in a Knight
8 shift of the signal due to deshielding of the lithium nuclei.⁴⁴ This can occur due to a larger cluster size
9 and would lead to a higher chemical shift of the ^7Li NMR signal. In terms of conductivity, increasingly
10 large clusters become more and more metallic. This results in effective chemical shifts closer to the
11 signal of lithium metal than to the GIC peak.⁴⁴ The second possible explanation originates from the low
12 graphitic structure of HCmicro. According to Tatsumi et al., the chemical shift of lithium clusters formed
13 in HC is determined by the chemical exchange between clusters in microcavities and GICs. It is
14 consequently moved to lower chemical shifts at room temperature while it splits into two peaks
15 at $-30\text{ }^\circ\text{C}$.^{22,33,34} The cluster signal for HC pore filling at temperatures below $-30\text{ }^\circ\text{C}$ can be found at a
16 chemical shift of approximately 180 ppm, which is in good agreement with the chemical shift of the
17 herein depicted ^7Li NMR signal at room temperature. Lithiated HCmicro might lack this shift due to the
18 minor content of ordered graphite domains, which was pointed out earlier by TEM measurements.
19 Further low temperature NMR measurements are required at this point to undoubtedly explain the
20 observed signal. However, it can be concluded that lithium clusters exist in the lithiated HCmicro
21 material, and that the lithium formation inside the HCmicro-electrode differs from the configuration in
22 HCs.

23

24 **Small Angle X-ray Scattering (SAXS) of lithiated HCmicro**

25 Further investigation on the HCmicro-electrode powder via SAXS measurement in sealed capillaries
26 revealed a change of the scattering profile before and after lithiation (Figure 5). Therefore, the HCmicro-
27 electrode was measured in the pristine and the lithiated stage discharged until $750\text{ mAh g}^{-1}_{\text{HCmicro}}$ after
28 pre-cycling with one initial formation cycle between 0.01 and 2 V. The obtained scattering profiles show
29 a lowered intensity between 1 and 8 nm^{-1} scattering vector for the lithiated HCmicro-electrode, which
30 implies lower contribution of the scattering of single and aggregated micropores to the overall scattering.
31 The difference in scattering intensity is also confirmed by measurements at various spots of the samples
32 revealing identical scattering. This indicates a loss in microporosity due to lithium insertion inside the
33 pores. A corresponding insertion mechanism has been described by Stevens et al. for lithium insertion
34 in hard carbon material.⁴²



1
 2 **Figure 5: SAXS analysis of HCmicro.** SAXS profiles of pristine (black) and lithiated HCmicro-
 3 electrode (blue) after pre-cycling in a half-cell vs. lithium metal between 0.01 and 2 V with a lithiation
 4 capacity of 750 mAh g⁻¹_{HCmicro}.

5
 6 Based on these findings we can assume that the lithium gathers inside the microporosity of the HCmicro
 7 during electrochemical lithiation. We therefore propose a unique lithiation mechanism for HCmicro in
 8 all solid-state batteries as follows (Figure 6).

9
 10 **Proposal for lithium insertion mechanism**

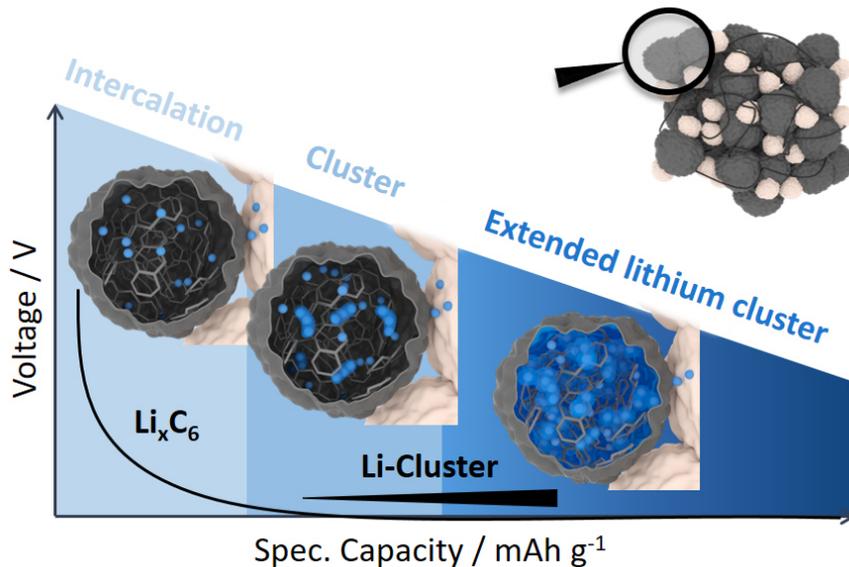
11 The second plateau observed in the delithiation step of both carbons in the constant current and the
 12 constant voltage experiments is a unique observation for the HCmicro, which shows no plateau capacity
 13 in liquid-electrolyte experiments.^{8,50} A theoretical study on a graphene hetero structure with large
 14 interlayer distance by Bijoy and Murugan predicted the stabilization of extended lithium clusters
 15 between the layers with a slightly expanded interlayer distance of 3.4 Å.⁵¹ In combination with our
 16 studies, this suggests the existence of such lithium clusters stabilized between the pore walls of
 17 HCmicro. The spatial pore-pore connection in HCmicro furthermore leads to connected pore voids and
 18 enables the formation of extended lithium clusters and advanced lithium storage compared to HC
 19 although comparable results concerning the size of micropores for both carbons were obtained in SAXS
 20 measurements. In larger pores, more clusters can combine. Thereby, they also eventually gain
 21 characteristics of bulk lithium, which is suggested by the existence of a short linear plateau at the
 22 beginning of the delithiation step and by the bulk lithium signal in ⁷Li NMR despite the missing of a
 23 typical plating dip in the voltage profiles of the HCmicro.

24 Hence, we assign the second plateau of the electrochemical investigation of the half-cells to the
 25 delithiation of lithium clusters inside the porosity of the carbons. The higher capacity reached in this
 26 region for HCmicro-electrode compared to the HC-electrode gives further evidence for a higher amount
 27 of lithium nuclei assembled in its cluster structures as concluded from ⁷Li MAS NMR measurements.
 28 Consequently, we propose that the formation of extended lithium clusters in the pore-pore connected,

1 accessible microporous system of the HCmicro is facilitated by the combination with the herein
2 employed solid-state electrolyte.

3

4 In summary, the following mechanism for lithium insertion into HCmicro in an all solid-state set-up is
5 proposed (Figure 6). As established in literature for hard carbons, the lithium ions firstly adsorb on
6 defects or edges of the carbon surface in the sloping region of the potential curve. In the following
7 potential plateau intercalation of Li^+ in the small graphite-like domains of the HCmicro takes place.⁵²
8 Subsequently, lithium ions deposited at the edge of graphite-like domains and on pore walls start to form
9 clusters which will extend in size upon further lithiation.^{24,53} At a certain point, the growth of lithium
10 metal will take place either when cluster size reaches high numbers of nuclei resulting in rearrangement,
11 or eventually, the lithium may even start plating on the outer shell of the carbon when the porosity is
12 completely filled. However, lithium metal formation occurs very homogeneous and no short-circuits
13 were observed for HCmicro-electrode since there is a smooth transition from cluster to bulk lithium. We
14 therefore name the herein presented approach a carbon/lithium hybrid anode-concept.



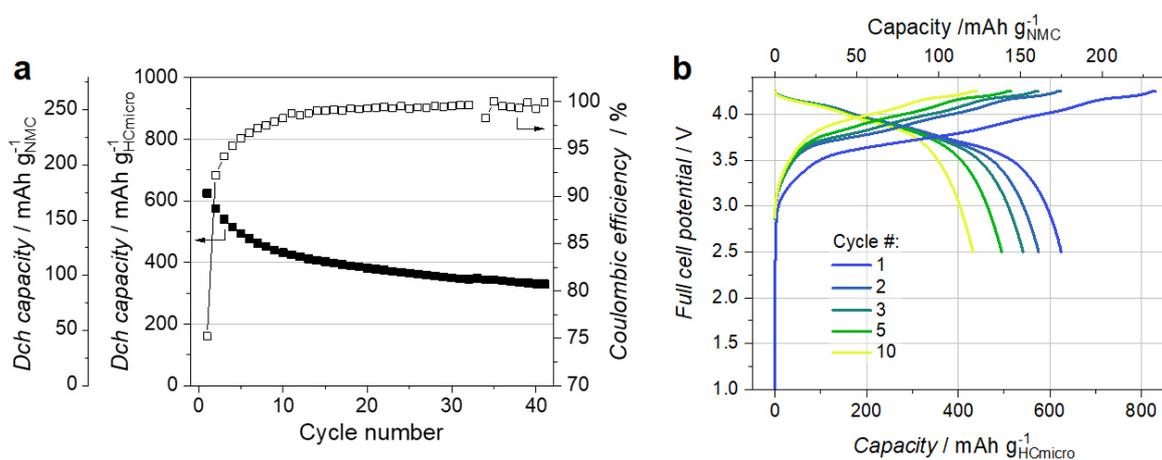
15
16 **Figure 6: Proposed mechanism of lithium insertion in microporous carbon as anode material in**
17 **all solid-state batteries.** Scheme divided into 3 phases: the intercalation of lithium, cluster formation
18 as known from hard carbon lithiation and the formation of extended lithium clusters as special feature
19 of the HCmicro anode material in all-solid-state electrolyte.

20
21

22 Stable full-cell performance vs. NMC cathode

23 The excellent performance of the half-cells motivated us to demonstrate the first full-cell results
24 combining the described carbon anode concept with a suitable cathode material (Figure 7 and
25 Supplementary Figure 4). The full-cells consisting of a HCmicro-electrode anode and a nickel-rich
26 NMC ($\text{LiNi}_{0.9}\text{Mn}_{0.05}\text{Co}_{0.05}\text{O}_2$) cathode with $\text{Li}_6\text{PS}_5\text{Cl}$ electrolyte exhibit relatively stable reversible

1 cycling performance over 40 cycles with coulombic efficiencies exceeding 98% in 10th cycle and at least
 2 75% initial CE. The capacity of the cells starts with 174 mAh g⁻¹_{NMC} concluding with 92 mAh g⁻¹_{NMC} in
 3 40th cycle. Based on the weight of the anode active material, this capacity results in 625 mAh g⁻¹_{HCmicro}
 4 for the 1st cycle. The average voltage was calculated via the measured energy and capacity values of
 5 specific cycle step of the cell with 3.76 V in first discharge improving to 3.79 V in 10th cycle and
 6 continuing at this value until 40th cycle (see Supplementary Note 1). This is a clear improvement
 7 compared to the average voltage of 3.55 V in first discharge for a HC-electrode full-cell with comparable
 8 composition continued with 3.53 V for 3rd discharge (see Supplementary Figure 4). It should be
 9 mentioned that these results are the very first experiments on highly microporous carbons with reversible
 10 capacity as high as 1000 mAh g⁻¹_{carbon} in combination with argyrodite-type solid electrolyte and with a
 11 nickel-rich cathode. Especially, these electrodes were assembled without any pre-lithiation of the carbon
 12 anode or other additional lithium content. Therefore, all of the lithium capacity derives from the dry film
 13 NMC cathode⁵⁴ and there is no additional lithium to replace irreversibly reacted lithium from side
 14 reactions in the first cycles. As a consequence, these results underline the reversible (de)lithiation
 15 concept of the HCmicro anode. So far, no further optimization was conducted regarding the balancing
 16 of electrodes, the particle size and shape of the carbon or other commonly used procedures for
 17 commercial battery improvement. Consequently, these results are of high value and are expected to be
 18 further improved, e.g., by pre-lithiation of the carbon via chemical or physical approaches.^{55,56}
 19 Theoretical calculation of the investigated ASSB cell revealed projected gravimetric and volumetric
 20 energy densities of 443 Wh kg⁻¹ and 1001 Wh L⁻¹ for the complete cell stack at n/p = 1 as utilized in the
 21 experiment assuming an SE layer thickness of 30 μm (detailed calculation see Supplementary Table 1
 22 and 2 plus Notes).



24
 25 **Figure 7: Electrochemical characterization in full-cells.** Discharge (Dch) capacities calculated based
 26 on HCmicro (anode) and NMC content (cathode) and coulombic efficiency of HCmicro/NMC all solid-
 27 state full-cell (a) as well as voltage profiles of the first cycles shown in capacity per NMC (upper axis)
 28 and per HCmicro (lower axis) (b).

29
 30

1 **Conclusion**

2 Summarizing our findings, we were able to show a carbon/lithium hybrid anode-concept based on the
3 microporous carbon anode material TiC-CDC (HCmicro) in an all solid-state battery to obtain high and,
4 above all, reversible lithiation capacities of $1000 \text{ mAh g}^{-1}_{\text{HCmicro}}$ with initial CE as high as 70% in half-
5 cells.

6 The advancement regarding the cell concept presented herein is the long plateau region in the potential
7 profile of the half-cell measurements at very low potential vs. Li/Li^+ , which is a desired characteristic
8 in order to significantly enhance full-cell energy density. Our investigations of the lithiation mechanism
9 revealed the formation of lithium clusters inside the open pore system of HCmicro by ^7Li MAS NMR
10 cluster signal and gave evidence for a distinct lithium formation mechanism compared to hard carbon
11 lithium clusters indicated by the characteristic chemical shift of the formed species. The unique
12 combination of a porous carbon with the solid electrolyte enables the storage of highly dispersed and
13 stabilized quasi-metallic lithium, which results in a highly reversible cell performance at room
14 temperature. Finally, such a hybrid lithium-HCmicro anode concept was successfully combined and
15 cycled 40 times vs. a nickel-rich NMC cathode. Without any extra lithium source beside the NMC
16 cathode material, these full-cells obtained $174 \text{ mAh g}^{-1}_{\text{NMC}}$ in 1st discharge and more than half of the
17 initial capacity remained in 40th cycle. The average full-cell potential improved significantly compared
18 with the HC full-cell by more than 0.2 V to a value of 3.76 V for the HCmicro full-cell, which leads to
19 a projected energy density as high as 443 Wh kg^{-1} .

20 This work demonstrates the potential of porous carbons as 3-dimensional framework architectures for
21 the stabilization of metallic or cluster-type lithium. The possibility to tune pore size, pore volume and
22 pore functionalization of carbon materials and their combination with solid electrolytes is a promising
23 option for the production of high capacity anodes for future high energy density prototype cells.

24

25 **Methods**

26 *Materials*

27 The carbon materials used for electrode preparation – hard carbon (HC, Kuraray Co., Ltd.), carbide-
28 derived carbon (TiC-CDC-1000, HCmicro) and graphite powder – were dried for 12 h at $200 \text{ }^\circ\text{C}$ under
29 vacuum before use. The TiC-CDC-1000 (HCmicro) was synthesized at Technical University Dresden
30 from TiC particles (Sigma Aldrich, -325 mesh, 98%) via chlorination process at $1000 \text{ }^\circ\text{C}$ as previously
31 described by Borchardt et al.⁵⁷ Argyrodite type solid electrolyte ($\text{Li}_6\text{PS}_5\text{Cl}$, SE) with approx. $3 \text{ }\mu\text{m}$ and
32 $15 \text{ }\mu\text{m}$ particle diameter was utilized as received for electrode batch preparation and SE pellet in cell
33 stacks, respectively. Lithium metal foil was purchased with a thickness of $50 \text{ }\mu\text{m}$ from China Energy
34 Lithium Co., Ltd. and was prepared in an Ar-filled glove box via punching out disks with 13 mm
35 diameter. $\text{Li}_2\text{O-ZrO}_2$ (LZO) coated $\text{LiNi}_{0.9}\text{Co}_{0.05}\text{Mn}_{0.05}\text{O}_2$ (NMC) was prepared by the sol-gel method
36 based on ZrO_2 coating as stated in a previous publication.⁵⁴

1 All further material handling and cell preparation was conducted under inert gas atmosphere in an Ar-
2 filled glovebox with moisture and air content below 0.01 ppm.

3

4 *Electrode materials preparation*

5 To prepare the anode composite electrode powders further named as HCmicro-, HC- and graphite-
6 electrode, the dried carbon - HCmicro, HC and graphite, respectively - was mixed manually with
7 conductive carbon additive (CNF, CNF_PR-25-XT-HHT, Pyrograf), and SE (Li₆PS₅Cl, 3 μm particle
8 diameter) in the mass ratio of 60:5:35 for 30 min in an agate mortar.

9 NMC-cathodes for full-cell experiments were prepared via dry-film processing as described by Hippauf
10 et al.⁵⁴ with 16.1 mg_{AM}/cm² loading of LZO-coated NMC with a mass ratio of 85:2:13 of NMC:CNF:SE.

11

12 *Half-cell and full-cell preparation*

13 The half-cells were prepared in a stainless steel outer casing with a polyoxymethylene liner by using a
14 die with a diameter of 13 mm. Therefore, a lithium foil with a diameter of 13 mm and 50 μm thickness
15 was arranged inside the die and SE powder (150 mg ±0.5 mg) was uniformly spread on top by a micro-
16 spatula. This composition was temporarily compressed and compacted into a pellet. Afterwards, the
17 composite powder HCmicro-, HC- or graphite-electrode, respectively, (7.37 mg ±0.2 mg) was
18 homogeneously distributed across the compacted electrolyte surface in the die and again compressed by
19 using a hydraulic press applying 4 tons for 30 s. The resulting areal active material loading of the half-
20 cell was 3.33 mg cm⁻². Before cell performance measurement, the cells were closed airtight inside a
21 pouch bag.

22 Full cells were prepared similar to half-cell preparation except for the lithium foil, which was replaced
23 by the NMC-cathode and was positioned centered on top of the SE pellet after the carbon-anode
24 preparation and the SE pellet formation.

25

26 *Electrochemical measurements*

27 All cells were stored for 5 hours after assembly before electrochemical measurement started. The cell
28 performance measurements were conducted on a battery tester CTS-Lab (BaSyTec, Germany). The half-
29 cells were discharged with 0.05 mA cm⁻² until a constant capacity of 1000 mAh g⁻¹ or cut off if going
30 below -0.02 V earlier followed by a 30-min-pause and a subsequent charging at the same areal current
31 density until 2 V. This procedure was repeated for 10 cycles.

32 The full-cells were cycled between 2.5 and 4.25 V with a constant voltage step at the end of each
33 charging until a cut-off current of 0.015 mA cm⁻². The areal current density was 0.05 mA cm⁻² as well.

34 Further electrochemical experiments were conducted on a VSP-300 (Bio-Logic, France). Constant
35 voltage measurements (ConVol) were conducted with pre-cycling between 0.01 and 2 V with a current
36 density of 0.05 mA cm⁻² for 2 times. A constant current (CC) step in discharge with 0.05 mA cm⁻² until

1 0 V and subsequent ConVol step at 0 V until a cut-off current of $-7.5 \mu\text{A cm}^{-2}$ followed for 3 cycles with
2 in between charging at 0.05 mA cm^{-2} to 2 V.

3 Cyclovoltammetry (CV) procedure was conducted with 0.01 mV s^{-1} between the upper cut-off voltage
4 at 1 V and changing lower cut-off voltages of 10, 2, 0 and -5 mV each for 4 cycles. The I-step duration
5 was set to 50%.

6

7 *Materials characterization*

8 Powder X-ray diffraction (XRD) patterns were measured on a Bruker D8 in Bragg-Brentano geometry
9 in a 2θ range of $10\text{-}70^\circ$ with a resolution of 0.03° using $\text{CuK}\alpha$ radiation ($\lambda=0.15418 \text{ nm}$) and a NaI
10 scintillation detector. The samples were placed on a horizontal silicon single crystal holder.

11 Nitrogen physisorption isotherms were measured via low-pressure nitrogen physisorption at 77 K with
12 an Autosorb 1C apparatus (Quantachrome), using 10-20 mg of activated sample. Activation was
13 conducted under vacuum for 12 h at 200°C after a heating period of 2 h on a Belprep Vac II. The
14 multipoint BET equation ($p/p_0 = 0.05\text{-}0.2$) served for calculation of the specific surface area, whereas
15 pore volumes were estimated from the volume of adsorbed nitrogen at $p/p_0 = 0.97$ for the micro- and
16 mesoporous content. The quenched-solid density functional theory (QSDFT) for nitrogen at 77 K on
17 carbon with slit/cylindrical pores (adsorption branch) was utilized to retrieve the pore size distributions
18 (PSDs).

19 For Raman measurements, a Renishaw inVia microscope with an excitation laser wavelength of 514 nm
20 at 5% laser power ($0.1 \text{ mW } \mu\text{m}^{-3}$) and 50-fold magnification was used measuring between 100 and
21 3500 cm^{-1} for two times 30 s. The intensity ratio $I(\text{D})/I(\text{G})$ was calculated from the fitting of G-Peak via
22 Breit-Wigner-Fano and D-Peak with Lorentz fitting with a linear base line analysed from 1200 cm^{-1} to
23 1750 cm^{-1} .

24 Small-angle X-ray scattering was measured on a Bruker Nanostar 2 device using $\text{CuK}\alpha$ radiation in
25 transmission geometry with 279 mm distance between sample and detector at a vacuum level of
26 approximately 0.02 mbar. Prior to each measurement, samples were filled into borosilicate capillaries
27 inside the glovebox, temporarily closed with polymer foil and finally sealed by melting the glass,
28 immediately after extraction from the glovebox.

29 Solid-state ^7Li MAS NMR experiments were carried out on a BRUKER Avance NEO 300 MHz
30 spectrometer at a resonance frequency of 116.6 MHz with a commercial double resonance 2.5 MAS
31 NMR probe operating at a MAS frequency of 15 kHz. 32 Scans were accumulated. The pulse repetition
32 time was 60 s. SPINAL 1H-decoupling was applied during signal acquisition. The lithium chemical shift
33 was referenced with LiCl.

34 The TEM investigations were conducted using a double-Cs-corrected Jeol ARM200F, equipped with a
35 cold field emission gun and operated with an acceleration voltage of 80 kV as well as on a TEM JEM-
36 211, JEOL.

1 Scanning electron microscopy (SEM) was performed on a HITACHI SU8020 at 2.0 kV with a working
2 distance of 8.9 and 15.3 mm for HC and HCmicro, respectively. The samples were sputtered on a Q150R
3 ES (Quorum) with Au nanoparticles (≤ 10 nm) before SEM measurement.
4

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7 **Competing interests:**

8 The authors declare no competing financial or non-financial interests.

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10 **Supplementary Information:**

11 Supplementary Tables 1-2, Figures 1-4, Notes and references.