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Supporting Information

Towards 3D-Lithium Ion Microbatteries Based on Silicon/Graphite Blend Anodes Using a Dispenser Printing Technique

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Physiochemical Measurements

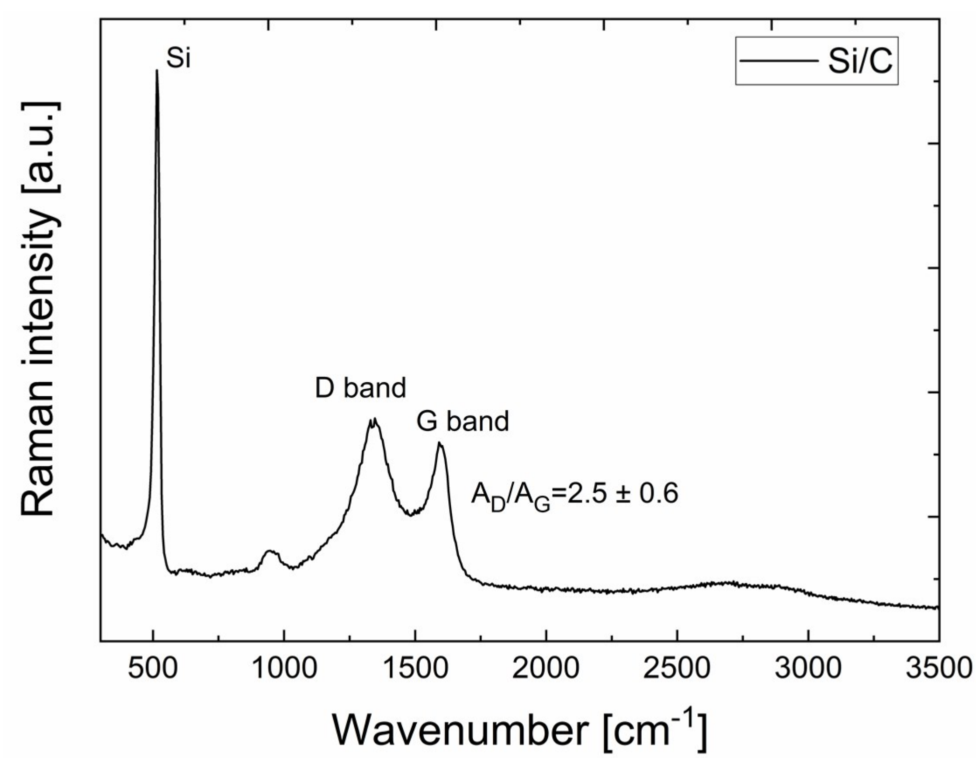

Figure S1: Raman spectra of Si/C anode material in the range between 300 and 3500 cm^{-1}.

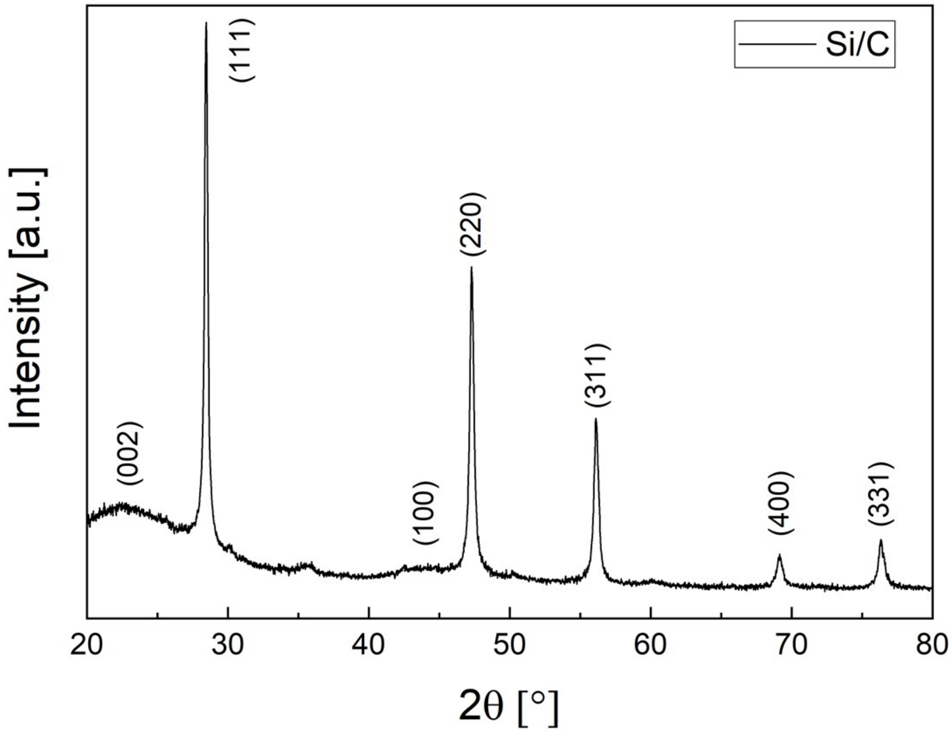

Figure S2: XRD pattern of Si/C anode material. The peaks refer to the reflection planes of the carbon and the silicon crystal.

Particle Size Distribution

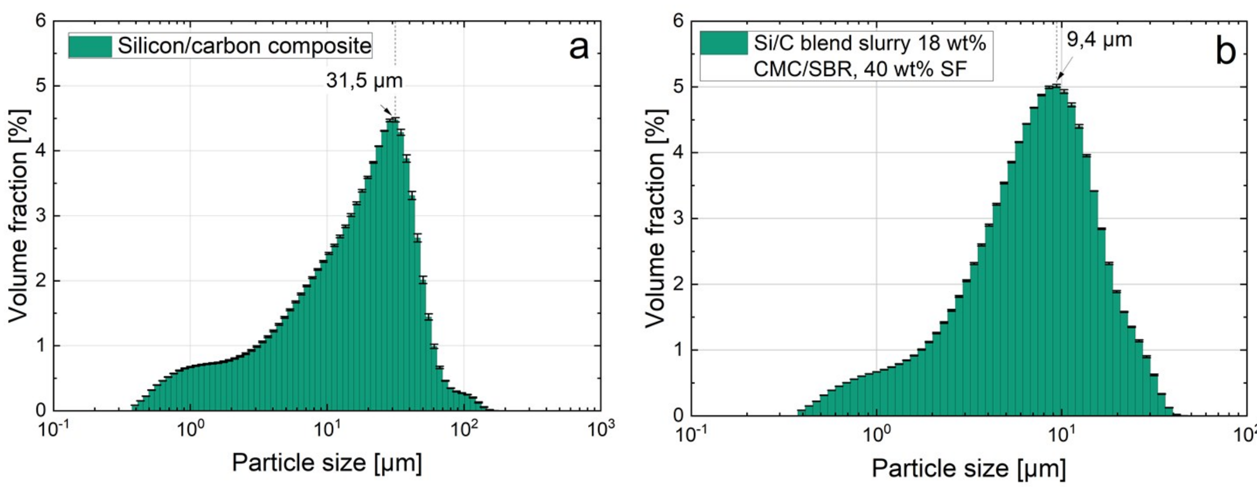

Figure S3 Particle size distribution of a) the Si/C composite after ball milling and b) a slurry containing 18 wt% CMC/SBR binder and 40 wt% solid fraction after the three roll process.

Electrochemical Measurements

Figure S4 shows the coulombic efficiencies (CE) of the Si/C graphite blend cells. The samples with 6 wt%, 12 wt%, 18 wt% and 24 wt% binder have a first cycle CE of 72.9 %, 74.2 %, 75.5 % and 76.0 %, respectively. Values of the second cycle CE are 96.3 %, 96.4 %, 96.7% and 97.0 %, respectively. At current rates of 2C and 4C the anode with 24 wt% binder shows CE values higher than 100%. Possible explanations for that behavior might be i) decomposition of electrolyte components, ii) formation of shunt resistances or iii) kinetic effects. Samples with lower amounts of binder reach their highest CE values between 99.6 % and 99.7 % at a current rate of 4C.

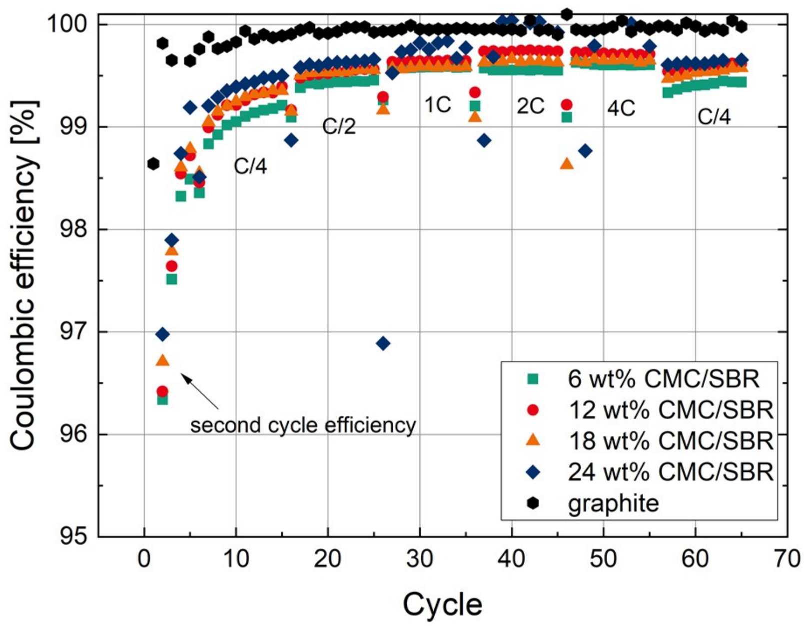

Figure S4: Coulombic efficiencies of Si/C graphite blend anodes in dependence of the binder and C-rate in CCCV cycling setup.

To investigate the resistance of the Si/C graphite blend cells in more detail the average ohmic drop values were measured and corresponding internal resistances calculated (see Figure S5 and corresponding voltage profiles Figure S6). Therefore, cells were first charged to 100 % SOC (1.5

V, U_1) and discharged for 1 s (U_2). The value of U_1-U_2 was defined as ohmic drop. Internal specific resistances were calculated using the following equation

$$R_{int} = \frac{(U_1 - U_2)}{I_{dis}} \tag{1}$$

where U_1 is the potential at 100% SOC, U_2 is the potential after 1 s of discharge and I_{dis} is the specific discharge current [1]. With increasing binder content and C-rate ohmic drop values increase which is commonly known and due to kinetical limitations of the anode. Furthermore it can be found that R_{int} values increase with increasing binder content at a specific C-rate. Thus, corresponding capacity losses (see Figure 6a) might be due to increased internal resistances caused by the electrically insulating properties of the binder. However, comparable low capacity values for the sample with 6 wt% binder cannot be explained in the same way and reasons for that remain unclear. With increasing current, internal resistances for all anodes decrease. This is obviously due to the predominant effect of the current increase (see equation 1). However, decreasing capacity values (see Figure 6a) are not expected to be affected by decreasing resistance. Although ohmic drop and resistance values are linked via equation 1 and ohmic drop behavior provides reliable explanations for decreasing capacity of the cells, internal resistance values evolve contrary to expectations.

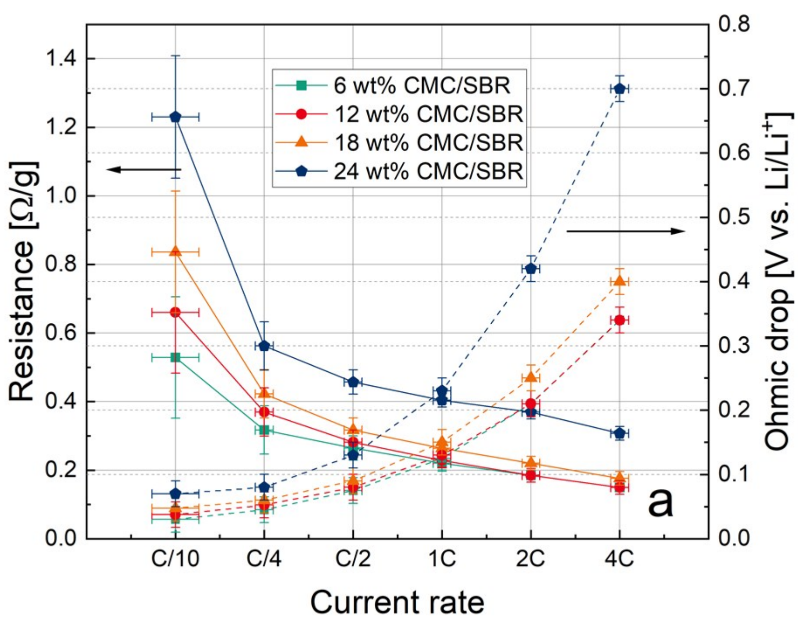

Figure S5: Ohmic drop of Si/C graphite blend anode based lithium metal cells between CC charge and CC discharge and corresponding internal resistance.

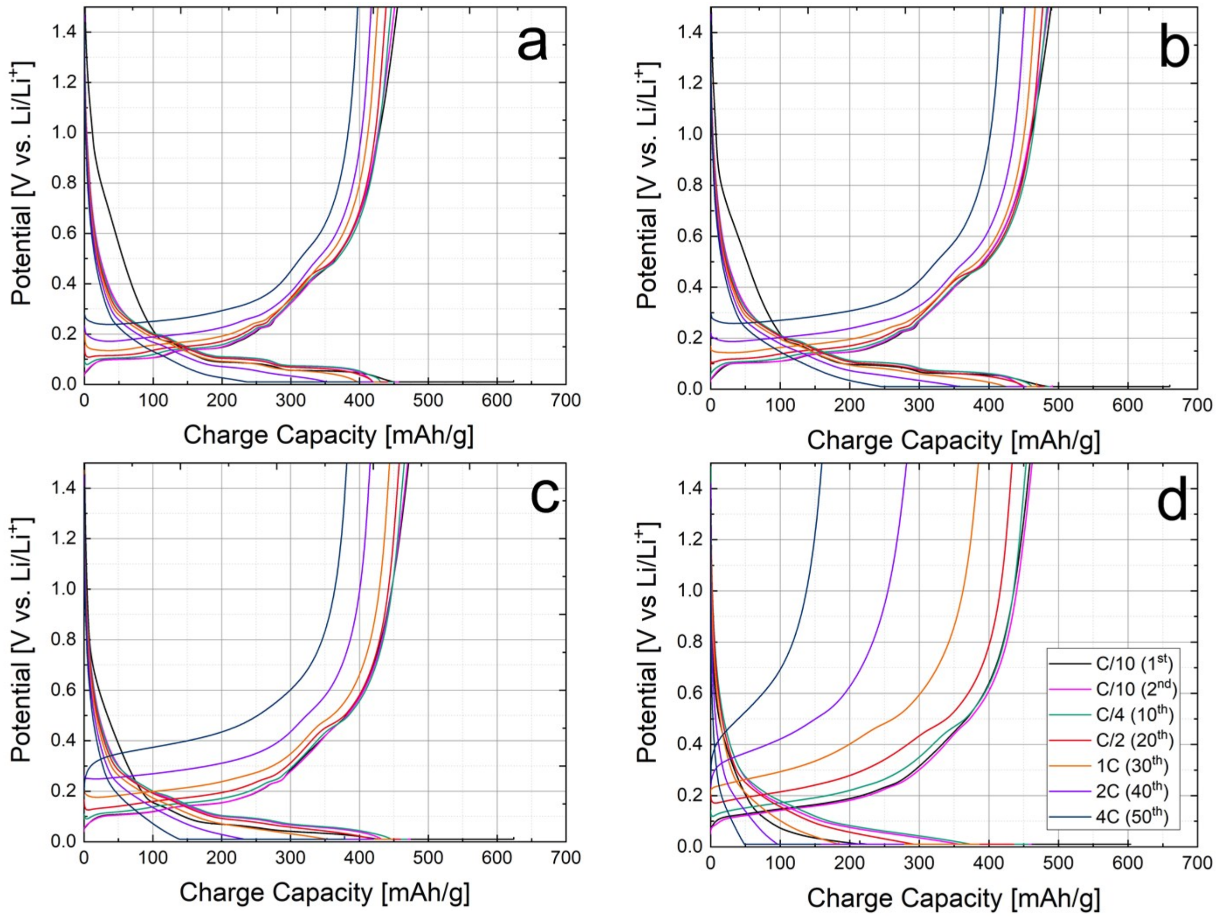

Figure S6: Voltage profile of Si/C Graphite blend anodes wit a) 6 wt%, b) 12 wt%, c) 18 wt% and d) 24 wt% CMC/SBR binder in dependence of the current rate. Legend is the same for d-a. Number of the cycle is given in parentheses.

References

[1] Zhao, S., Wu, F., Yang, L., et al.: ‘A measurement method for determination of dc internal resistance of batteries and supercapacitors’, Electrochemistry Communications, 2010, **12**, pp. 242–245