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Sodiated carbon: A reversible anode for the sodium-oxygen battery and route for the chemical synthesis of sodium superoxide (NaO_2)

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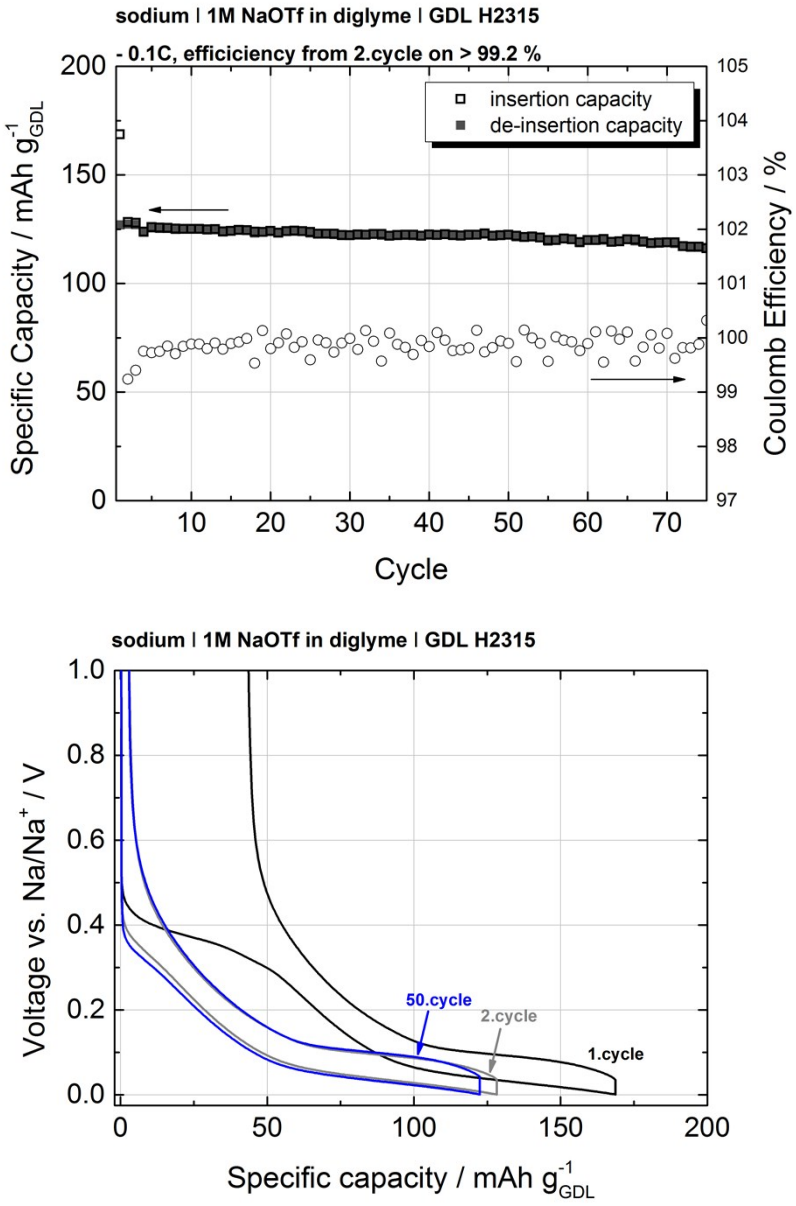

Figure S1: Voltage-capacity profiles for sodiation/de-sodiation of the GDL. After a first irreversible capacity of about q = 50 mAh·g^{-1}, the electrode reactions continue at around q = 125 mAh·g^{-1}with an average coulombic efficiency exceeding 99.2%.

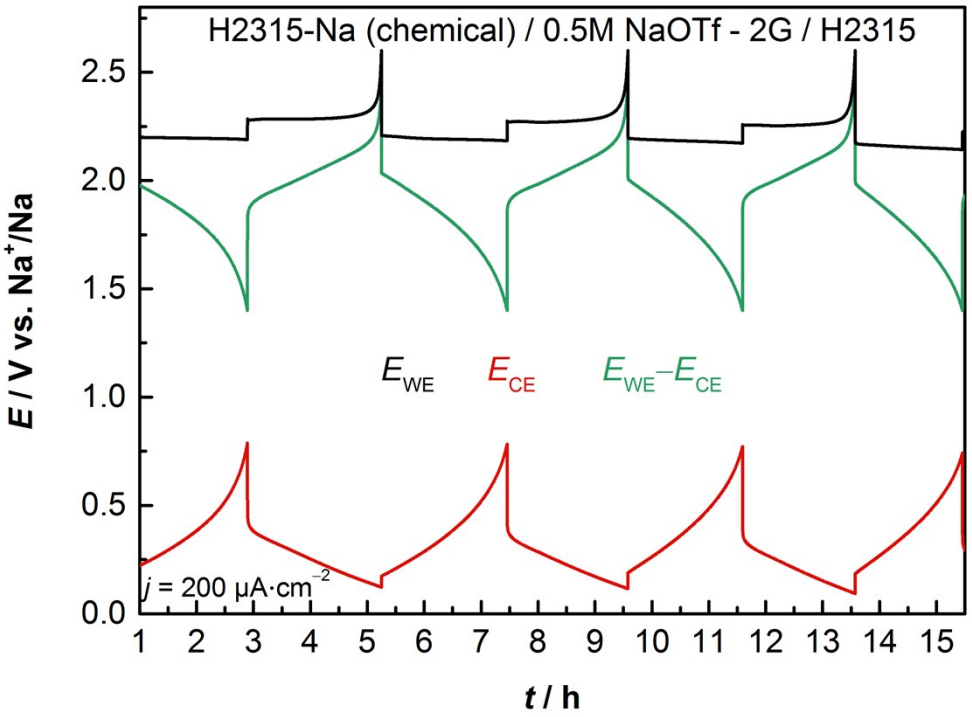

Figure S2: Galvanostatic cycling of a cell with a chemically sodiated carbon GDL as anode, and a GDL as oxygen cathode. The electrode potentials of both electrodes are recorded against a sodium reference electrode (three electrode configuration).. Black curve: working electrode, cathode GDL H2315; red curve: counter electrode, anode GDL H2315; green curve: two-electrode potential of the full cell. The activity of the cell proofs that the chemical sodiation of the carbon GDL was successful.

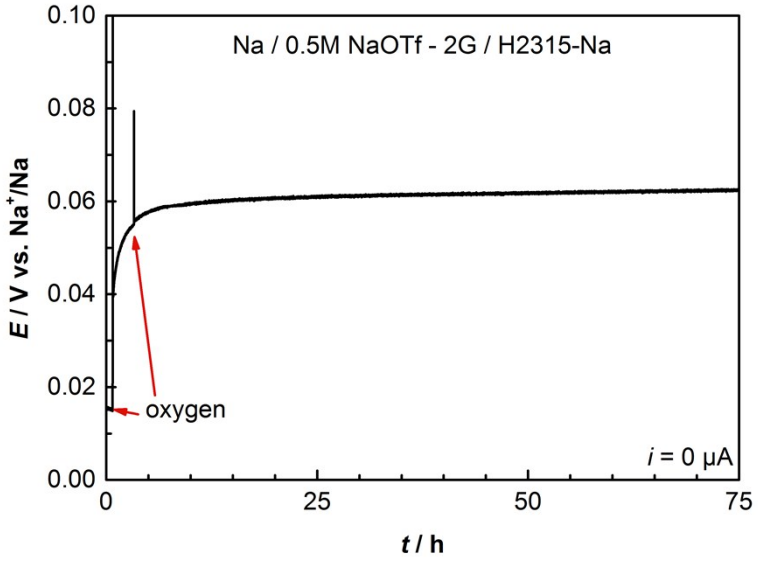

Figure S3: OCP measurement of a cell with the Na/C compound vs. a Na^+/Na electrode. At the marked points in the graph oxygen was flushed through the cell. As a result the potential increases. In oxygen atmosphere the potential is stable over more than 75 hours.

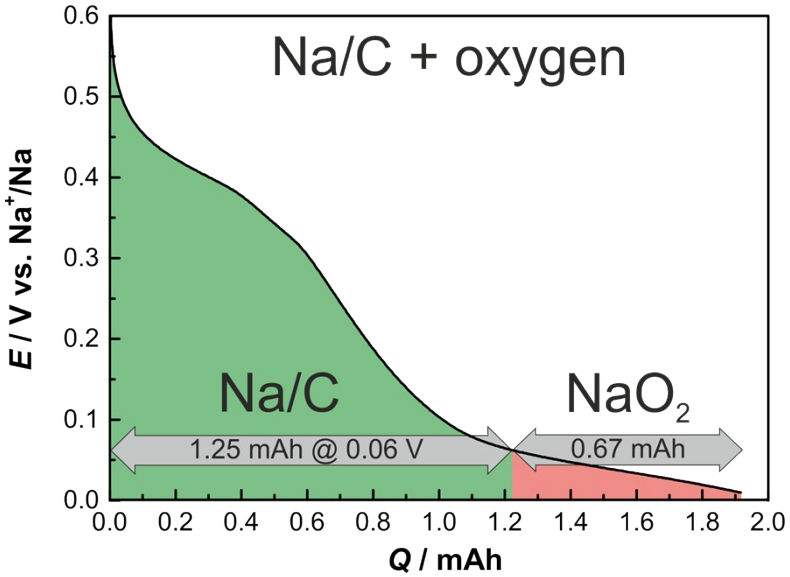

Figure S4: Graph visualizing regions of different reactivity of the Na/C insertion compound. The green area under the potential plot depicts the potential region with stable storage of sodium while the red area shows the potential region which is unstable against chemical reaction with oxygen. The Na/C insertion compound forms NaO_2 by direct chemical reaction if it has been loaded to potentials below E = +0.06 V (vs. Na^+/Na).

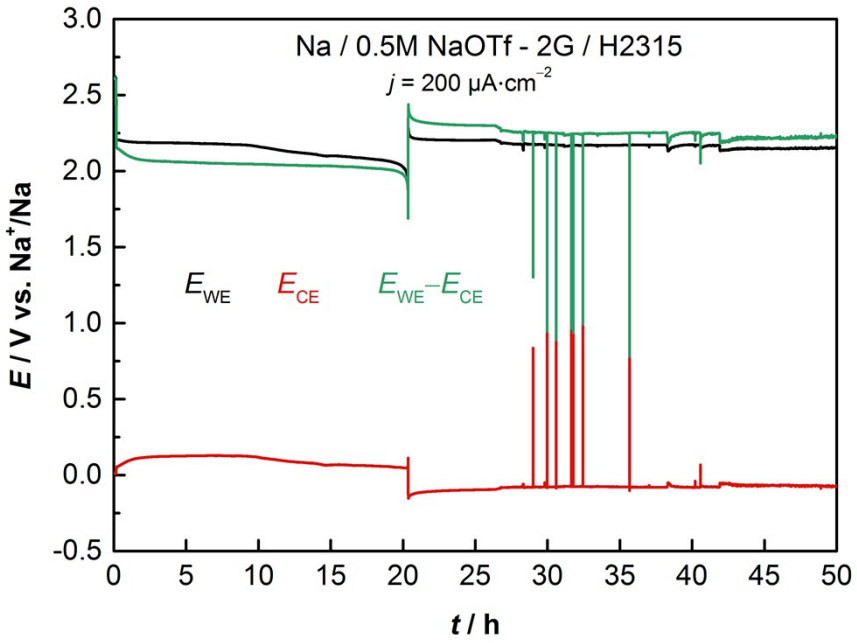

Figure S5: Potential-time series of a sodium-oxygen cell with dendrite formation during the first charge step. As the dendrite grew through the separator, both electrodes (anode and cathode) show potential break-downs.

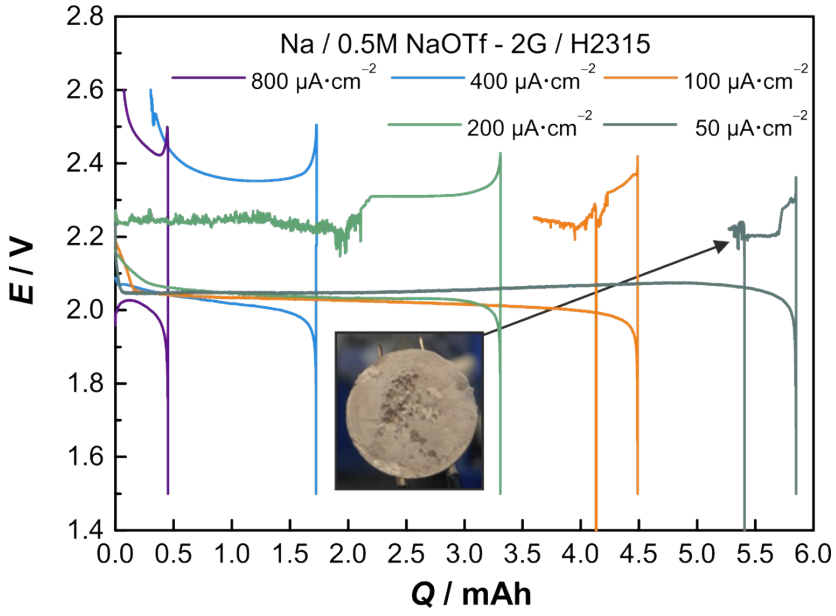

Figure S6: Rate capability of sodium-oxygen cells with sodium metal anode. In all cells dendrites occurred. The inset photograph shows the sodium anode of the cell cycled with j = 50 µA/cm².

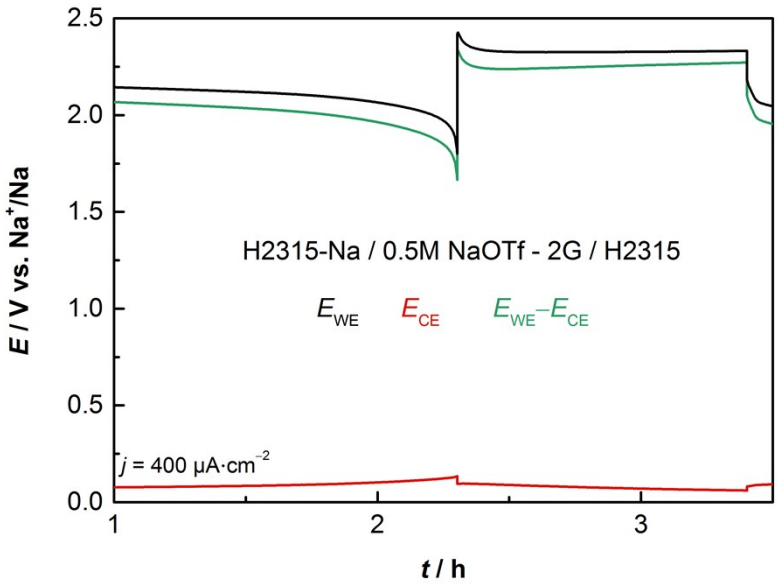

Figure S7: Potential-time profile of a cell with cathode limitation at high current densities. The red curve depicts the potential of the Na/C insertion anode, and the black curve depicts the potential of the GDL/oxygen cathode. It is obvious that the cathode is mainly responsible for the evolution of the cell voltage.

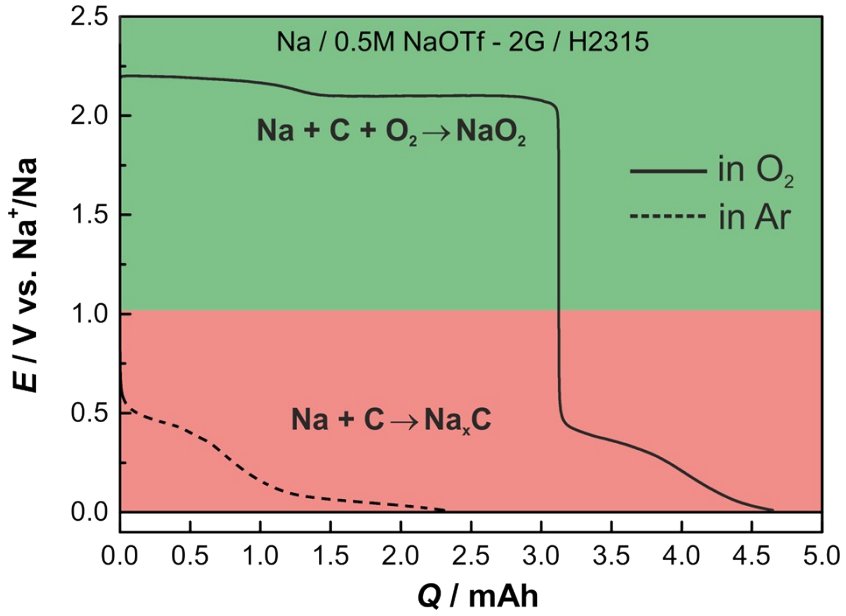

Figure S8: Potential-capacity profile for discharge of a Na/O_2 cell with and without oxygen. The lower cut-off potential was set to E_{limit} = 0.01 V and the current density was j = 200 µA·cm^{-2}. The green area depicts the potential region were NaO_2 is formed during discharge. The red area depicts the potential region were the Na/C compound is formed. In argon only the insertion compound can be formed as no oxygen is present for the superoxide reaction. However, in oxygen first the reaction to sodium superoxide takes place and second at potentials lower than E = 0.6 V also the insertion compound is formed. The potential describes the cathode potential. The insertion of sodium takes place on the cathode side if a metallic sodium anode is used.

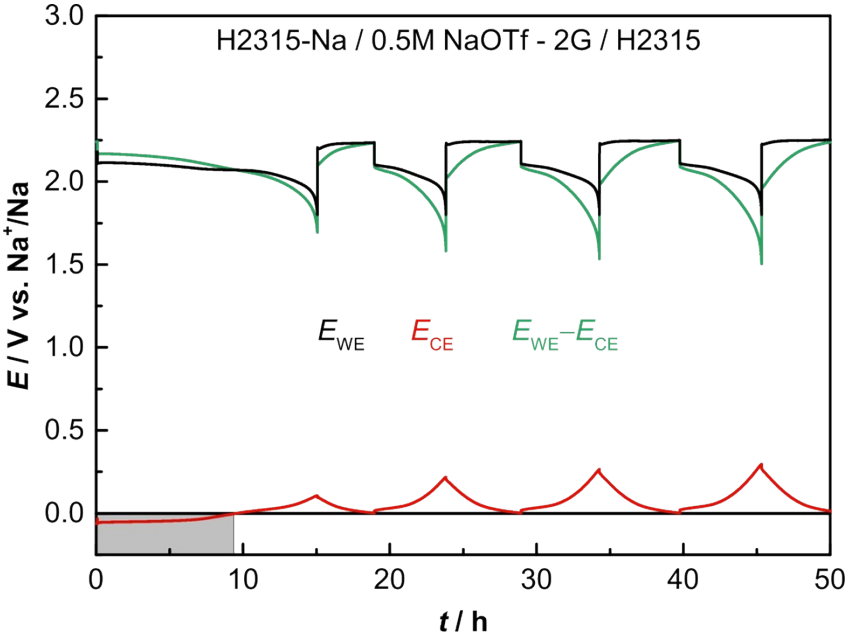

Figure S9: Detail of the subsequent galvanostatic cycling with three electrodes and controlled potentials for each electrode of the cell with prefilled NaO_2 GDL-cathode. The grey area depicts deposited sodium on the carbon anode. See Fig. 4. Cycling was conducted with cut-off potentials for each electrode. The anode was cycled between E = 0.01 V and E = 1 V; the cathode was cycled between E = 1.8 V and E = 2.6 V respectively. Black curve: working electrode, cathode GDL H2315; red curve: counter electrode, anode GDL H2315; green curve: two-electrode potential of the full cell.

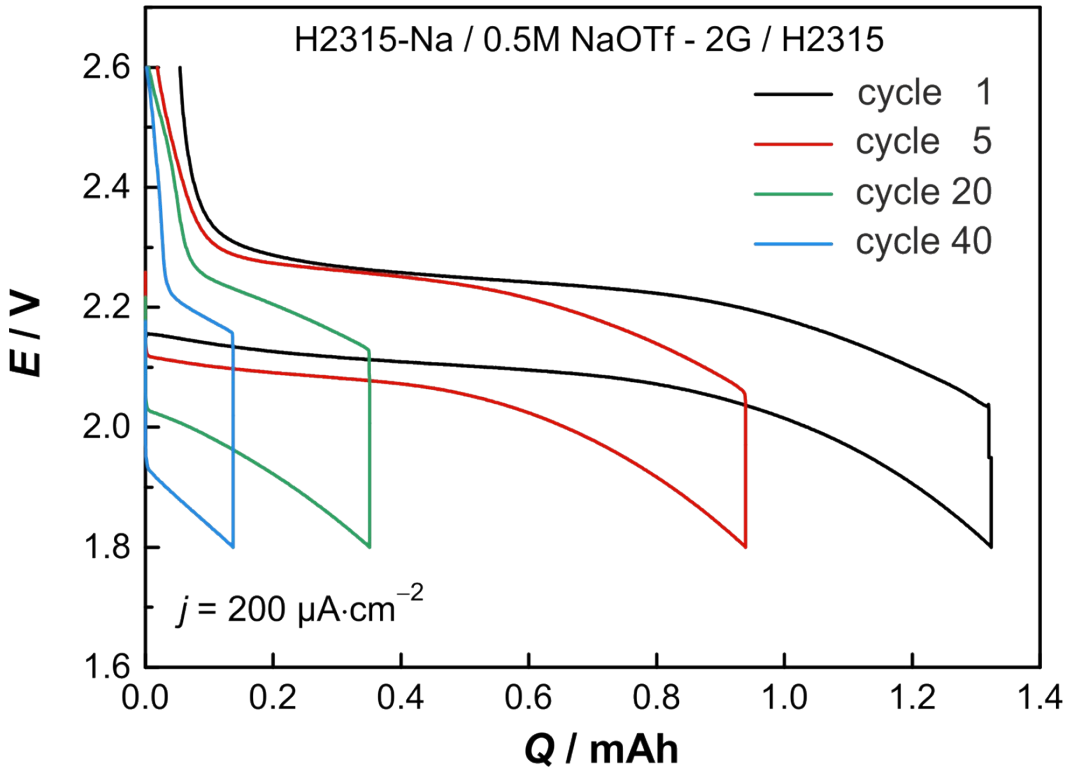

Figure S10: Discharge and Charge curves corresponding to Figure 3d.