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Supplementary Materials

Pulse Discharging of Sodium-Oxygen Batteries to Enhance Cathode Utilization

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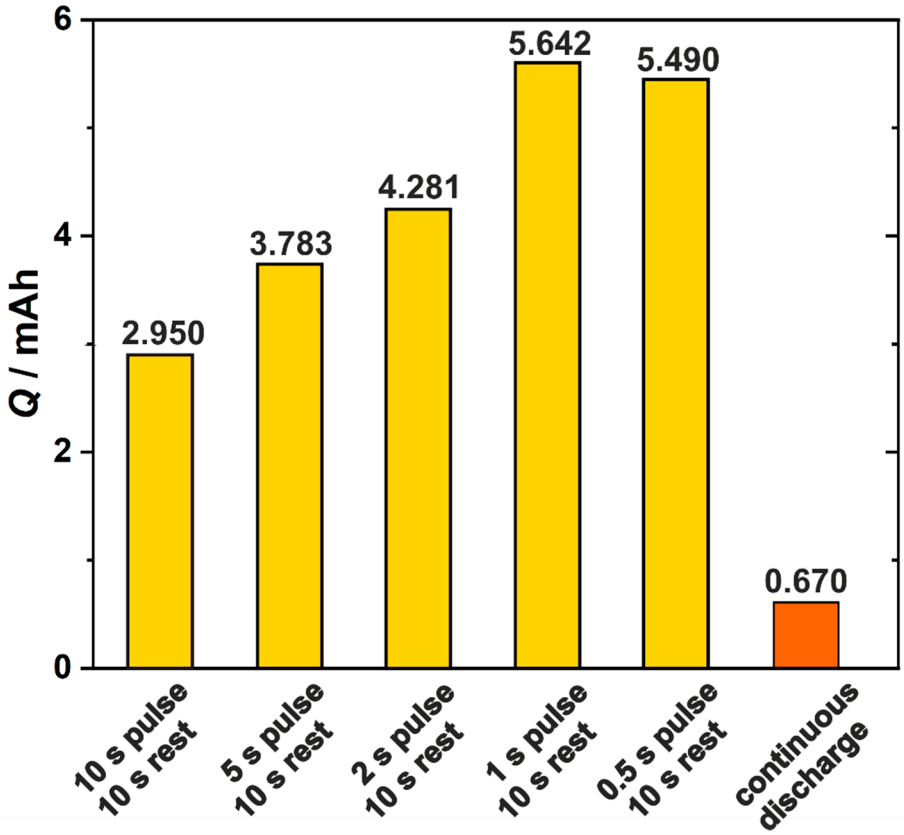

Figure S1. Comparison between different t_{rest}/t_{pulse} ratios for Na/O_2 batteries discharged at 500 µA cm^{-2} in the pulse discharging setting (yellow bars). The discharge capacity is higher for higher t_{rest}/t_{pulse} ratios until it stays constant at around 5 to 6 mAh. Additionally the discharge capacity for a continuously discharged Na/O_2 battery is shown (orange bar). In direct comparison, the pulse discharging leads to capacities that are approximately 10 times higher than the continuously discharged counterpart.

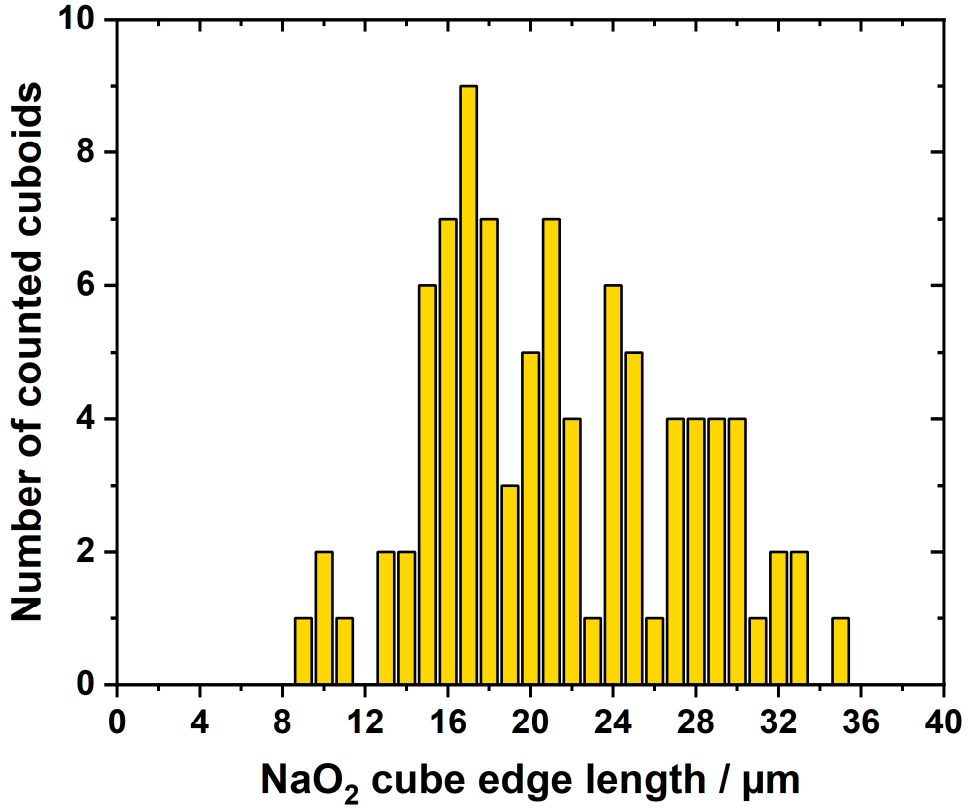

Figure S2. Histogram (counting by hand by means of a SEM image taken) for the cuboid edge length (CEL) of NaO_2 cuboids in the cathode after discharging a Na/O_2 battery intermittently at a current density of 500 µA cm^{-2}, using a resting time of 10 seconds and the pulse time with applied current to 1 second. The average CEL is determined to 21 µm, with the cuboid edge length ranging from approximately 9 µm up to 35 µm.

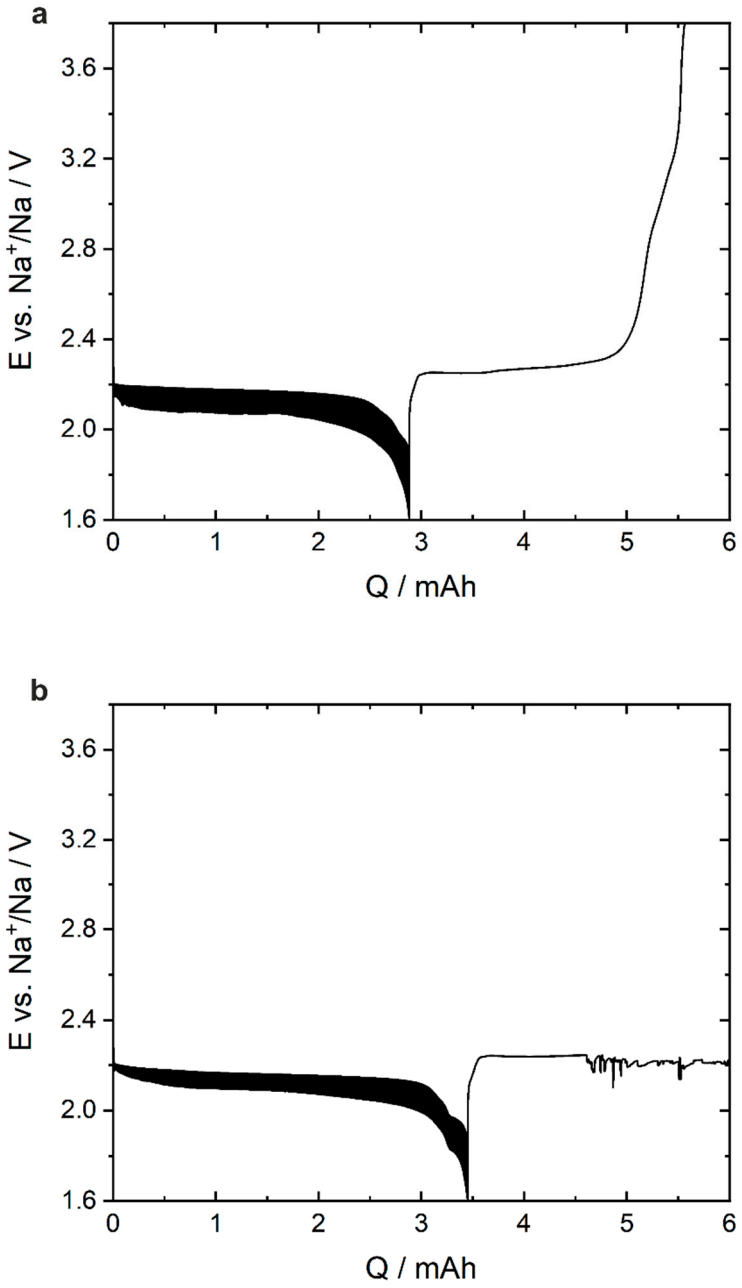

Figure S3. Pulse discharging and charging profiles of Na/O_2 batteries, that were discharged at 500 μA cm^{-2} by pulse discharging with 1 s pulse time and 10 s resting at OCV until the cut-off potential of 1.6 V vs Na^+/Na. a) The Na/O_2 battery shows a typical profile for the first charging cycle [1], reaching a coulomb efficiency of approximately 80 % for NaO_2 formation and decomposition. The battery in b) continuously shows drops in the potential beginning at approximately 4.6 mAh. This is a typical charging profile when thin dendrites are grown through the separators, connecting anode and cathode and inducing so-called "soft" short-circuits [2,3].

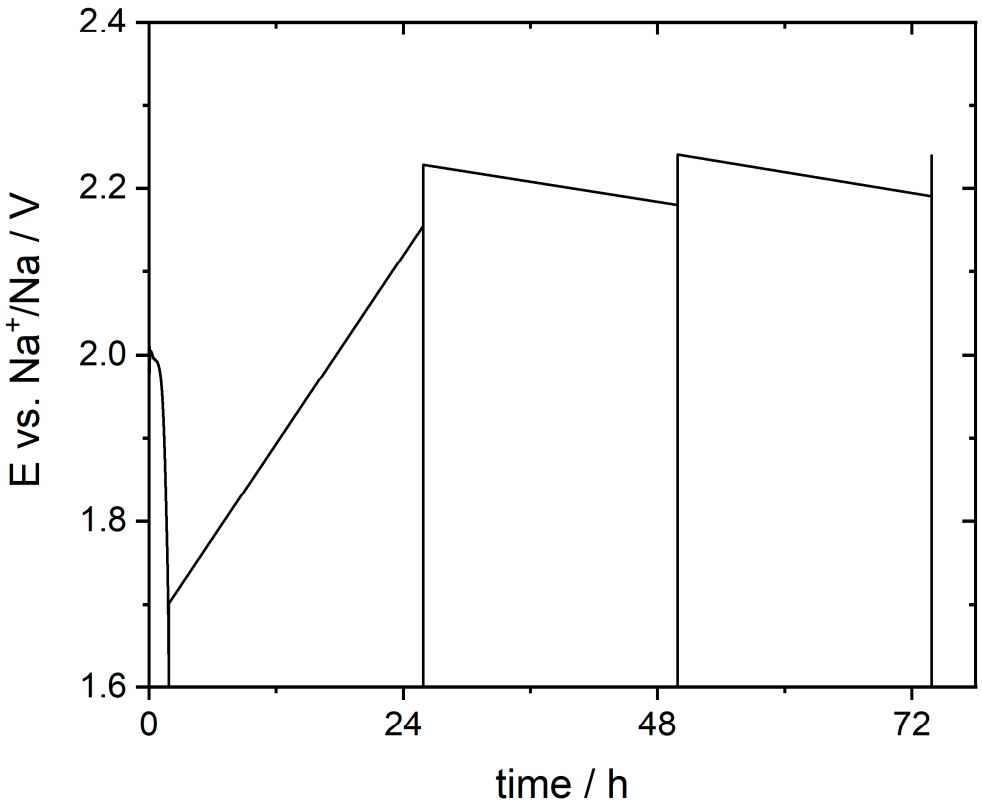

Figure S4. Long term OCV measurements of a discharged battery with additional discharge attempts after 24 h, 48 h and 72 h of OCV to elucidate if additional capacity can be obtained by the decomposition, and thus new active area for its deposition available in the cathode, of the discharge product NaO_2. After 24 h, 48 h and 72 h the current density can only be applied for less than 0.1 s due to the simultaneous drop of the potential below the chosen cut-off potential of 1.6 V vs. Na^+/Na, and it can be concluded that no additional active area was available for deposition of the discharge product.

1. Bender, C.L.; Hartmann, P.; Vračar, M.; Adelhelm, P.; Janek, J. On the Thermodynamics, the Role of the Carbon Cathode, and the Cycle Life of the Sodium Superoxide (NaO_2) Battery. *Adv. Energy Mater.* **2014**, 1301863–1301874. doi: 10.1002/aenm.201301863
2. Medenbach, L.; Bender, C.L.; Haas, R.; Mogwitz, B.; Pompe, C.; Adelhelm, P.; Schröder, D.; Janek, J. Origins of Dendrite Formation in Sodium–Oxygen Batteries and Possible Countermeasures. *Energy Technol.* **2017**, *5*, 2265 – 2274. doi: 10.1002/ente.201700326
3. Kreissl, J.J.A.; Langsdorf, D.; Tkachenko, B.A.; Schreiner, P.R.; Janek, J.; Schröder D. Incorporating Diamondoids as Electrolyte Additive in the Sodium Metal Anode to Mitigate Dendrite Growth. *ChemSusChem* **2020**, *13*, 2661– 2670. doi.org/10.1002/cssc.201903499