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Supplementary Information

Lithium-Air Battery Cathode Modification via an Unconventional Thermal Method Employing Borax

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Contents

S-1 Chemicals and Reagents

Lithium-air cathodes (H2315) were purchased from Freudenberg Group and used as received. Pharmaceutical borax was purchased from a local drug store with University ID. Polymeric microspheres were supplied by Polymer Standard Service (PSS), and 3-aminophenylboronic acid was purchased from abcr. Quartz tubes were obtained through the KIT University. Li-Foil and LiTFSI were purchased from Alfa Aesar. The ionic liquid *N*-methyl-*N*-propylpiperidinium bis(trifluoromethanesulfonyl)imide (PP13-TFSI) was purchased from Iolitec . The water level from the ionic liquid 48 ppm, before using we dried it further with lithium in an argon filled glove box.

S-2 Instrumentation Methods

Cyclic Voltammetry (CV). Cyclic Voltammetry measurements were conducted by a VSP potentiostat/galvanostat (Biologic, France) at 25 °C in the voltage range of 1.5-4.5 V with a 10 mV/s scan rate. Two-electrode Swagelok®-type test cells with a gas in- and outlet on the cathode site were assembled in an argon filled glove box using Li-foil as anode, 0.1M LiTFSI in PP13-TFSI as electrolyte and two glass microfiber filters (Whatmann®-GF/D 70mm Ø) as separator.

Energy-dispersive X-ray spectroscopy (EDX). EDX was conducted using a Quantax 400 System from Bruker. Due to the low X-ray energy of the elements boron (0.183 kV), carbon (0.277 kV) and fluorine (0.677 kV), the acceleration voltage was set to 10 keV during the EDX measurements. The duration of each measurement was at least 3 min for point measurements and 6 min for mappings. It has to be taken into account that with EDX spectroscopy it is not possible to detect lithium. Each sample was taken under investigation before and after cycling.

Scanning Electron Microscopy (SEM).

The lithium-air carbon cathodes were analyzed using a Zeiss Merlin with an acceleration voltage of 10 keV, a beam current of 168 pA and a working distance of 8 mm. For imaging the In-Lens-Detector was used. In all cases the sample was transferred into the SEM chamber without exposure to air by an in-house built transfer system.

X-Ray Photoelectron Spectroscopy (XPS). XPS Investigations were performed on a K-Alpha spectrometer (ThermoFisher Scientific, East Grinstead, U.K.) using a microfocused, monochromated Al Kα X-ray source (400 μm spot size). The kinetic energy of the electrons was measured by a 180° hemispherical energy analyzer operated in the constant analyzer energy mode (CAE) at 50 eV pass energy for elemental spectra. The photoelectrons were detected at an emission angle of 0° with respect to the normal of the sample surface. The K-Alpha charge compensation system was employed during analysis, using electrons of 8 eV energy and low-energy argon ions to prevent any localized charge build-up.

Data acquisition and processing using the Thermo Avantage software is described elsewhere.[1] The spectra were fitted with one or more Voigt profiles (BE uncertainty: (± 0.2 eV). The analyzer transmission function, Scofield sensitivity factors,[2] and effective attenuation lengths (EALs) for photoelectrons were applied for quantification. EALs were calculated using the standard TPP-2 M formalism.[3] All spectra were referenced to the C1s peak of graphite at 284,4 eV binding energy controlled by means of the well-known photoelectron peaks of metallic Cu, Ag, and Au, respectively.

S-3 Synthesis

Battery cathode modification process:

A quartz tube (1mm thick, 10mm diameter, ~40mm long) that is flame sealed on one end and open at the other end was used. The carbon cathode material (carbon cloth; 6mm diameter dye punched sample) was loaded into the quartz tube followed by the addition of a pre-weighed amount of dopant (e.g., borax). The quartz tube containing the cathode and dopant was subjected to high vacuum (1 x 10^{-2} – 1 x 10^{-3} mbar) and then sealed while under vacuum using a gas/air torch resulting in an average tube length of ~14mm. The tube was then taken to Majolika ceramic factory for firing. The firing process is conducted in a kiln designed for ceramic/pottery firing. Multiple quartz tubes (reaction vessels) were placed in the kiln while turned off at room temperature, then heated from rt-800 C, held @ 800 C for 0.5 hr, and then allowed to cool at ~ 100 ^{o}C/hr. The quartz tube was then opened using a diamond tool.

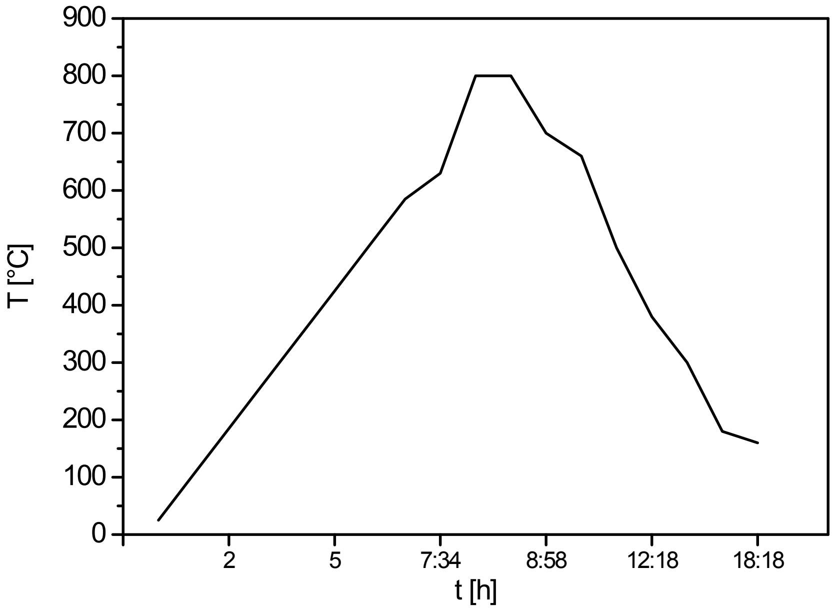

Fig S 1: Temperature profile of the heating process.

The possible influence of the water gas reaction and the Boudouard equilibrium:

In chemical transport reactions graphite is included to remove traces of up to 10^{-2} bar of H_2O through the following reactions [4]:

H_2O (g) + C (s) $\rightleftharpoons$ H_2 (g) + CO (g)

$\Delta_rH^0_{298}$ = 131.28 kJ·mol^{-1} $\Delta_rS^0_{298}$ = 134.08 J·mol^{-1}·K^{-1}

2 CO (g) $\rightleftharpoons$ C (s) + CO_2 (g)

$\Delta_rH^0_{298}$ = -172.5 kJ·mol^{-1} Δ_rS0_{298} = -175.9 J·mol^{-1}·K^{-1}

To take account of the presence of the graphite electrode, the thermochemical situation was recalculated with the help of these equilibria as well as the determination equation $p(H_2) = p(CO) + 2\ p(CO_2)$. The temperature dependence for the gas phase composition is presented in Figure SX (ampoule of 7 ml, loading 30 mg borax). As CO_2 or CO could not be detected inside the ampoules by gas phase Raman spectroscopy (excitation 532 nm, 1 W, Cobolt Samba DPSS laser, Dilor XY 800 Raman System, CCD camera), we assume, that the reactivity of graphite is negligible.

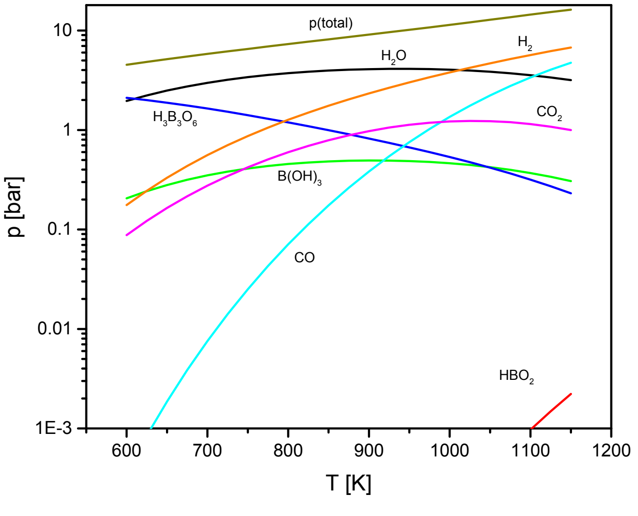

Fig S 2: Temperature dependence of the system B_2O_3 (l)/H_2O/C(s).

S-4 Supporting Figures

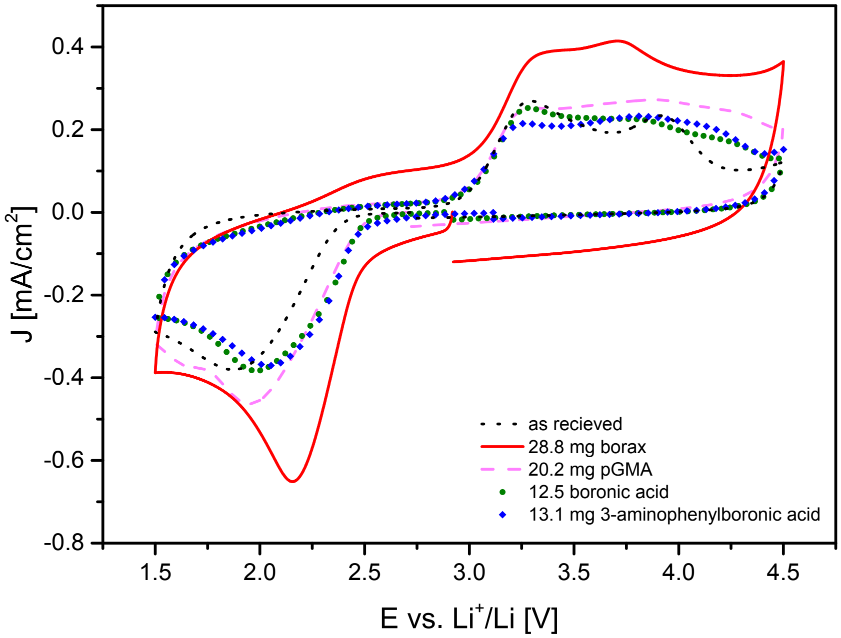

Fig S 3: CVs of different dopants on carbon at 10 mV s^{-1}. The surface area is compared to the geometric area of the cathode.

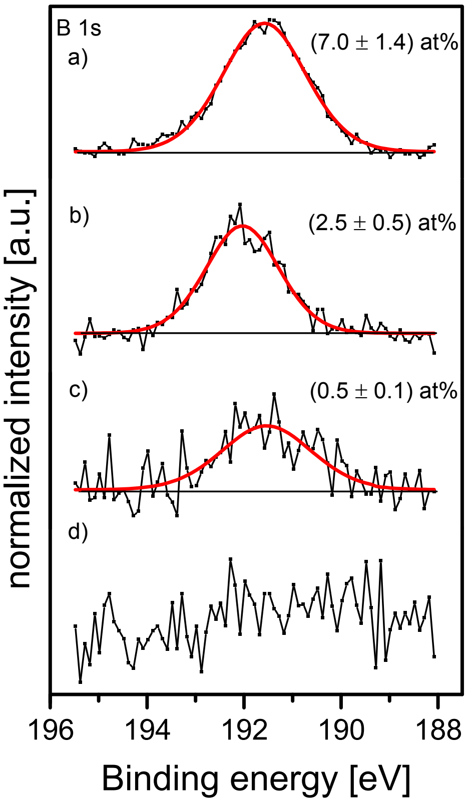

Fig S 4: XP B 1s spectra of carbon felt before cycling prepared with a) 30 mg b) 15 mg c) 5 mg d) 0 mg borax.

S-5 Supporting Tables

Table 1 – XPS: Quantitative analysis of the 5 mg Borax sample before and after cycling. The main elements are listed here.

atom	BE (eV)	Atomic % before cycling	Atomic % after cycling	
Li 1s	**55.2**	**-**	**19.0**	Li-O[5]
B 1s	**191.9**	**0.6**	**0.2**	B_2O_3[7]
C 1s	**284.4**	**83.7**	**32.3**	C-C graphitic[8]
C 1s	**285.0**	**9.7**	**9.8**	C-C aliphatic, C-H[8]
C 1s	**286.7**	**-**	**2.1**	C-O, C-N[8]
C 1s	**288.3**	**-**	**1.8**	C=O[8]
C 1s	**289.6**	**-**	**5.5**	O-C=O[8]
N 1s	**399.0**	**-**	**0.2**	
N 1s	**400.8**	**0.8**	**0.5**	
O 1s	**531.8**	**3.3**	**24.8**	C=O, Li_2O_2[6]
O 1s	**533.5**	**0.8**	**1.6**	C-O[8]
F1 s	**684.9**	**-**	**0.5**	LiF[5], [6]
F1s	**688.9**	**-**	**0.2**	C-F [6]
Na1s	**1071.9**	**1.1**	**-**	

For the evaluation of the ratio Li/O, we have to take account of the concentration of the both components C=O and O-C=O and submit them from the concentration of O 1s at 531,8 eV . These concentrations are not negligible. This leads to a ratio Li/O of 1.1.

Table 2 – XPS: quantitative analysis of the 15 mg borax sample before and after cycling.

atom	BE (eV)	Atomic % before cycling	Atomic % after cycling	
Li 1s	**54.7**	**-**	**28.6**	Li-O[5]
Li 1s	**56.9**	**-**	**3.6**	Li-F[5]
S 2p 3/2	**169.0**	**-**	**1.4**	S_{ox} (TFSI)
B 1s	**192.2**	**1.6**	**2.2**	B_2O_3[7]
B 1s	**194.1**	**-**	**0.7**	
C 1s	**284.4**	**77.7**	**10.5**	C-C graphitic[8]
C 1s	**285.0**	**8.2**	**6.9**	C-C aliphatic, C-H[8]
C 1s	**286.7**	**3.2**	**2.0**	C-O, C-N[8]
C 1s	**288.5**	**-**	**1.9**	C=O[8]
C 1s	**289.5**	**-**	**2.0**	O-C=O[8]
C 1s	**292.6**	**-**	**0.5**	C-F[6]
N 1s	**399.3**	**1.0**	**0.8**	
O 1s	**531.5**	**2.1**	**29.3**	C=O, Li_2O_2[6]
O 1s	**533.3**	**4.4**	**5.7**	C-O[8]
F 1s	**685.0**	**-**	**0.5**	LiF[5], [6]
F 1s	**688.8**	**-**	**2.1**	C-F [6]
Na1s	**1071.8**	**1.8**	**-**	

Here, on the same way we obtain a ratio Li/O of about: 1.1

Table 3 – XPS: quantitative analysis of the 30 mg borax sample before and after cyling.

atom	BE (eV)	Atomic % before cycling	Atomic % after cycling	
Li 1s	**54.8**	**-**	**21.4**	Li-O[5]
B 1s	**191.9**	**4.3**	**2.2**	B_2O_3[7]
C 1s	**284.4**	**77.8**	**31.5**	C-C graphitic[8]
C 1s	**285.0**	**2.9**	**7.6**	C-C aliphatic, C-H[8]
C 1s	**286.4**	**1.9**	**2.2**	C-O[8]
C 1s	**288.2**	**-**	**3.0**	C=O[8]
C 1s	**289.5**	**-**	**4.8**	O-C=O[8]
N 1s	**400.9**	**0.9**	**0.8**	
O 1s	**531.4**	**6.0**	**25.6**	C=O, Li_2O_2[6]
O 1s	**533.2**	**3.7**	**1.1**	C-O[8]
F 1s	**684.6**	**-**	**1.0**	LiF[5], [6]
F 1s	**688.5**	**-**	**0.4**	C-F [6]
Na1s	**1071.9**	**2.5**	**-**	

The ratio Li/O is here estimated to be 1.2.

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