# Supplementary information

**Table S1.** Structural parameters for $Li_6CuB_4O_{10}$ deduced from the Rietveld refinement of the synchrotron X-Ray diffraction pattern at 300 K.

| **Space Group *P* -1** | | | | | |
|---|---|---|---|---|---|
| *a*=4.821340(3) Å, *b*=9.234549(7) Å, *c*=13.964087(11) Å, $\alpha$=104.31439(5) °, $\beta$=96.21839(5)°, $\gamma$=94.57957(5)° | | | | | |
| *V*=595.195(1) Å$^3$ Z=3 | | | | | |
| **Atom** | **Wyckoff site** | ***x*** | ***y*** | ***z*** | **B(Å$^2$)** |
| B1 | 2*i* | 0.0852(19) | 0.4463(9) | 0.3336(7) | 0.39(14) |
| B2 | 2*i* | 0.1779(20) | 0.6796(10) | 0.4822(7) | 0.65(16) |
| B3 | 2*i* | 0.190(2) | 0.6607(10) | 0.1849(7) | 1.31(19) |
| B4 | 2*i* | 0.276(2) | 0.8972(10) | 0.3284(7) | 1.15(19) |
| B5 | 2*i* | 0.4190(20) | 0.7715(9) | 0.9908(7) | 0.66(17) |
| B6 | 2*i* | 0.4720(19) | 0.0004(9) | 0.1452(6) | 0.20(15) |
| Cu1 | 1*a* | 0 | 0 | 0 | 0.55(3) |
| Cu2 | 2*i* | 0.3000(2) | 0.31614(10) | 0.67137(8) | 0.43(2) |
| Li1 | 2*i* | 0.038(2) | 0.8018(12) | 0.8149(9) | -0.08(20) |
| Li2 | 2*i* | 0.068(4) | 0.3786(17) | 0.0345(12) | 3.2(4) |
| Li3 | 2*i* | 0.078(3) | 0.0713(14) | 0.8176(10) | 2.5(3) |
| Li4 | 2*i* | 0.221(3) | 0.9290(15) | 0.6293(10) | 1.7(3) |
| Li5 | 2*i* | 0.333(3) | 0.1367(12) | 0.4883(9) | 0.3(2) |
| Li6 | 2*i* | 0.368(3) | 0.4314(12) | 0.9148(9) | 1.0(2) |
| Li7 | 2*i* | 0.370(2) | 0.1719(12) | 0.3115(9) | 0.9(2) |
| Li8 | 2*i* | 0.414(3) | 0.5709(13) | 0.6101(9) | 1.8(3) |
| Li9 | 2*i* | 0.475(3) | 0.3997(14) | 0.1973(9) | 1.9(3) |
| O1 | 2*i* | 0.0246(10) | 0.5885(5) | 0.0998(4) | 0.55(10) |
| O2 | 2*i* | 0.0668(10) | 0.2575(5) | 0.5419(3) | 0.60(10) |
| O3 | 2*i* | 0.1071(10) | 0.7874(5) | 0.2506(3) | 0.26(9) |
| O4 | 2*i* | 0.1604(11) | 0.8056(5) | 0.9530(4) | 0.74(10) |
| O5 | 2*i* | 0.1579(10) | 0.0242(5) | 0.3609(3) | 0.26(9) |
| O6 | 2*i* | 0.1917(10) | 0.5242(5) | 0.6976(4) | 0.47(9) |
| O7 | 2*i* | 0.1846(9) | 0.0295(5) | 0.1315(3) | 0.13(8) |
| O8 | 2*i* | 0.2232(10) | 0.3413(5) | 0.2815(3) | 0.40(9) |
| O9 | 2*i* | 0.2392(11) | 0.5498(5) | 0.4203(4) | 0.55(10) |
| O10 | 2*i* | 0.3505(10) | 0.7487(5) | 0.5606(4) | 0.17(9) |

| | | | | | |
|---|---|---|---|---|---|
| O11 | 2*i* | 0.3435(11) | 0.9223(5) | 0.7707(4) | 0.22(10) |
| O12 | 2*i* | 0.4361(10) | 0.1228(5) | 0.9209(3) | 0.03(9) |
| O13 | 2*i* | 0.4692(11) | 0.1276(5) | 0.6251(4) | 0.48(9) |
| O14 | 2*i* | 0.4751(11) | 0.3536(5) | 0.0435(4) | 0.97(12) |
| O15 | 2*i* | 0.4624(10) | 0.6166(5) | 0.2042(3) | 0.24(8) |

**Table S2.** Structural parameters for $Li_6CuB_4O_{10}$ deduced from the DFT calculations.

| | **a (Å)** | **b (Å)** | **c (Å)** | **α (°)** | **β (°)** | **γ (°)** | **V (Å³)** |
|---|---|---|---|---|---|---|---|
| **Pristine DFT + U** | 4.8849 (1.2%) | 9.3465 (1.3%) | 14.1005 (0.7%) | 104.789 (0.4%) | 97.1720 (0.9%) | 93.6110 (0.9%) | 614.56 (2.9%) |

**Tab S3**: Lattice parameters and the corresponding voltage of $Li_6CuB_4O_{10}$ during galvanostatic charge and following discharge.

| | **a (Å)** | **b (Å)** | **c (Å)** | **α (°)** | **β (°)** | **γ (°)** | **V (Å³)** |
|---|---|---|---|---|---|---|---|
| **Charged 4.5V** | 4.837(5) | 9.119(5) | 14.088(5) | 104.082(5) | 96.936(5) | 94.115(5) | 595.052(5) |
| **Discharged 1.0V** | 4.829(5) | 9.251(5) | 14.021(5) | 104.36(5) | 96.538(5) | 94.472(5) | 599.244(5) |

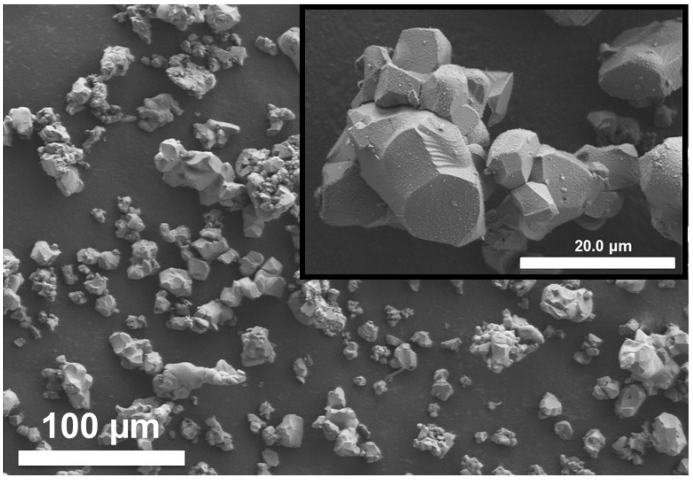


Figure S1: Representative SEM image of $Li_6CuB_4O_{10}$ particles after solid state synthesis.

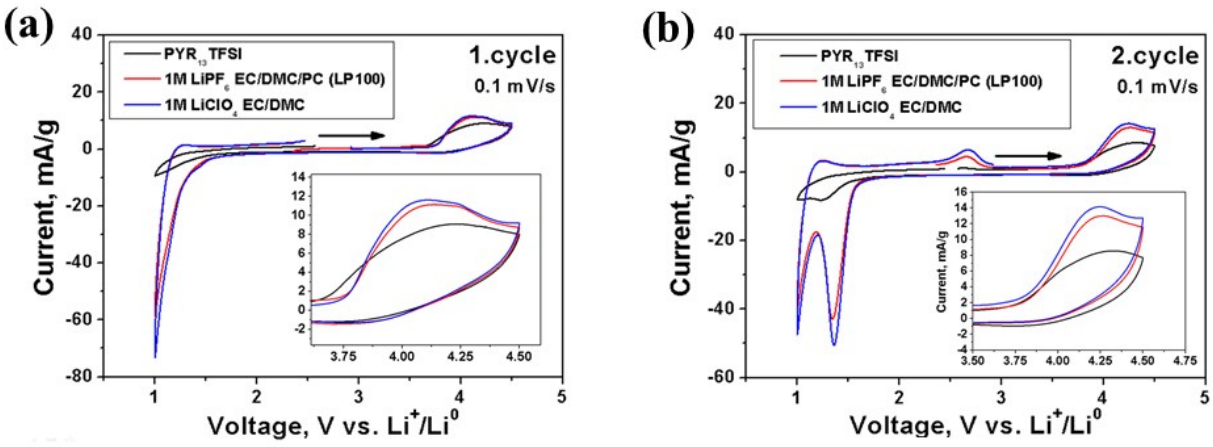


Figure S2: Cyclic voltammetry of $Li/Li_6CuB_4O_{10}$ half cells in different electrolytes in a potential window from 4.5-1.0 V vs. $Li^+/Li^0$ with a scan speed of 0.1 mV/s for the first (a) and second (b) cycle. Inset show the differences in anodic current due to electrolyte oxidation.

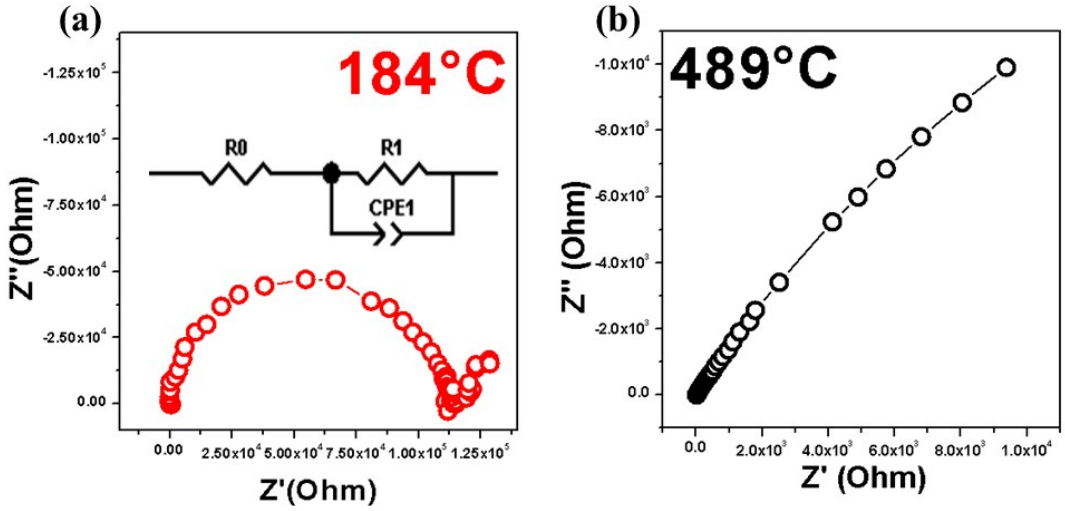


Figure S3: Complex a.c. impedance spectra for $Li_6CuB_4O_{10}$ measured at 184°C (a) and at 489°C (b) .

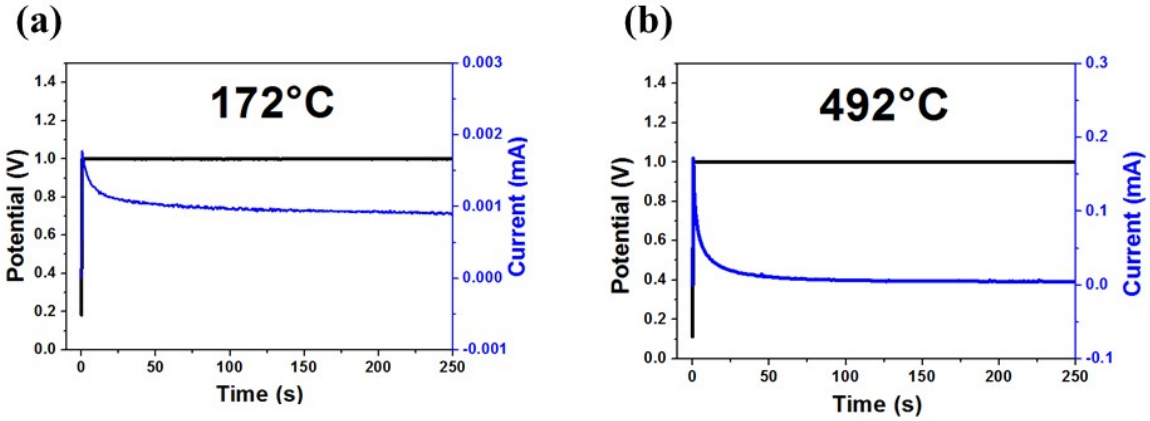


Figure S4: D.c. polarization measurements for $Li_6CuB_4O_{10}$ measured at 172°C (a) and at 492°C (b).