**Revisit Electrolyte Chemistry of Hard Carbon in Ether for Na Storage**

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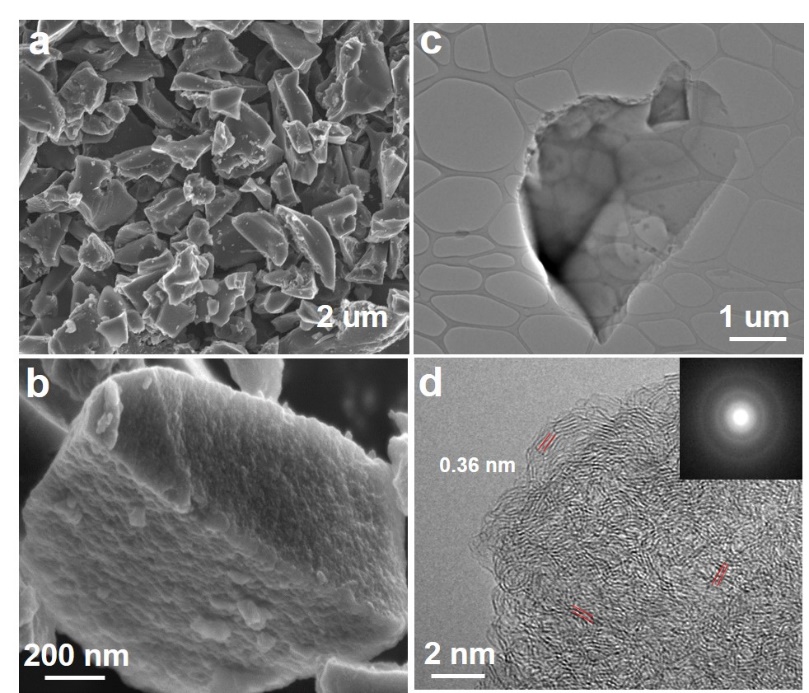
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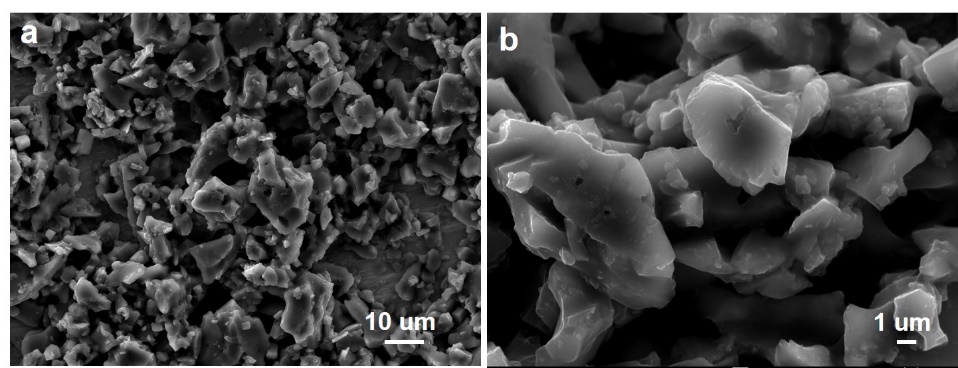
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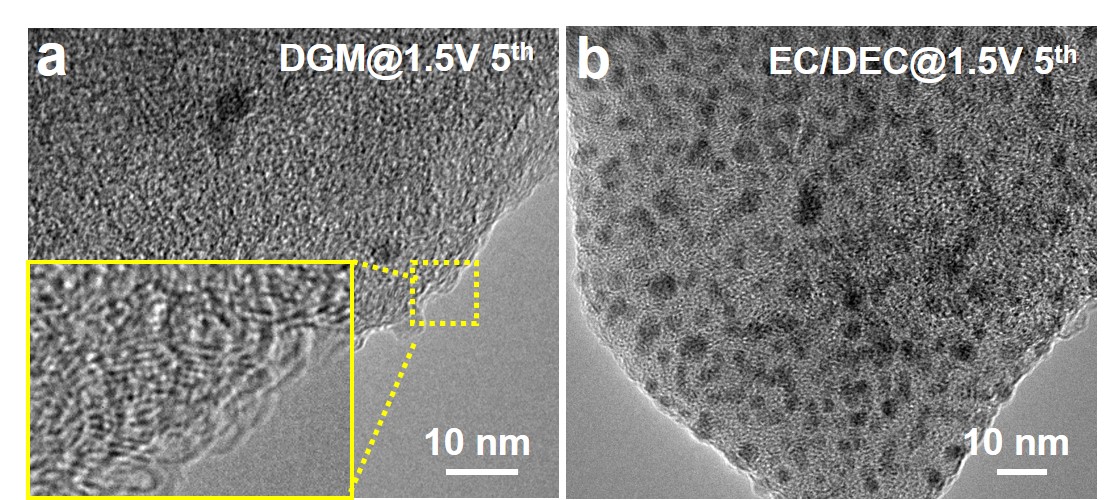
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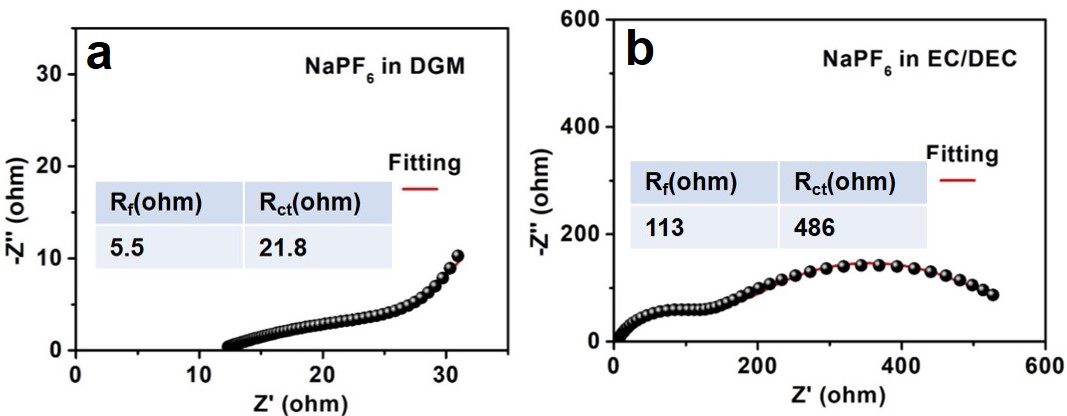
**Figure S1. Morphology of hard carbon.** (a, b) FESEM images, (c) TEM image, (d) HRTEM image.



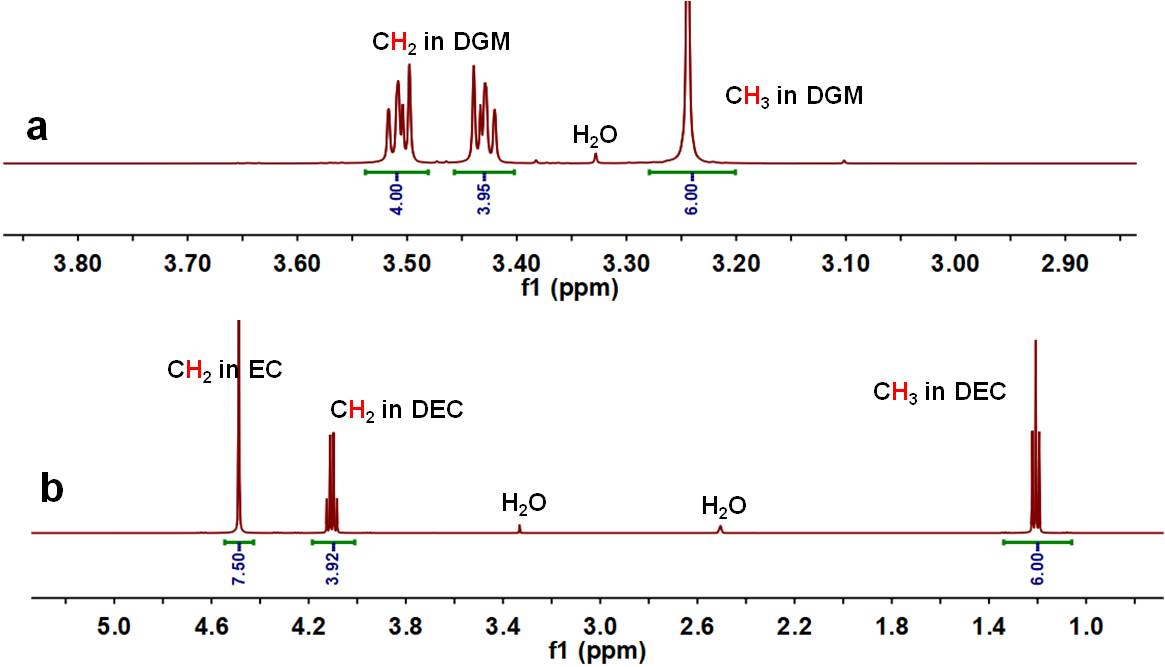
**Figure S2.** (a, b) *Ex-situ* FESEM of hard carbon after 3500 cycles in DGM.



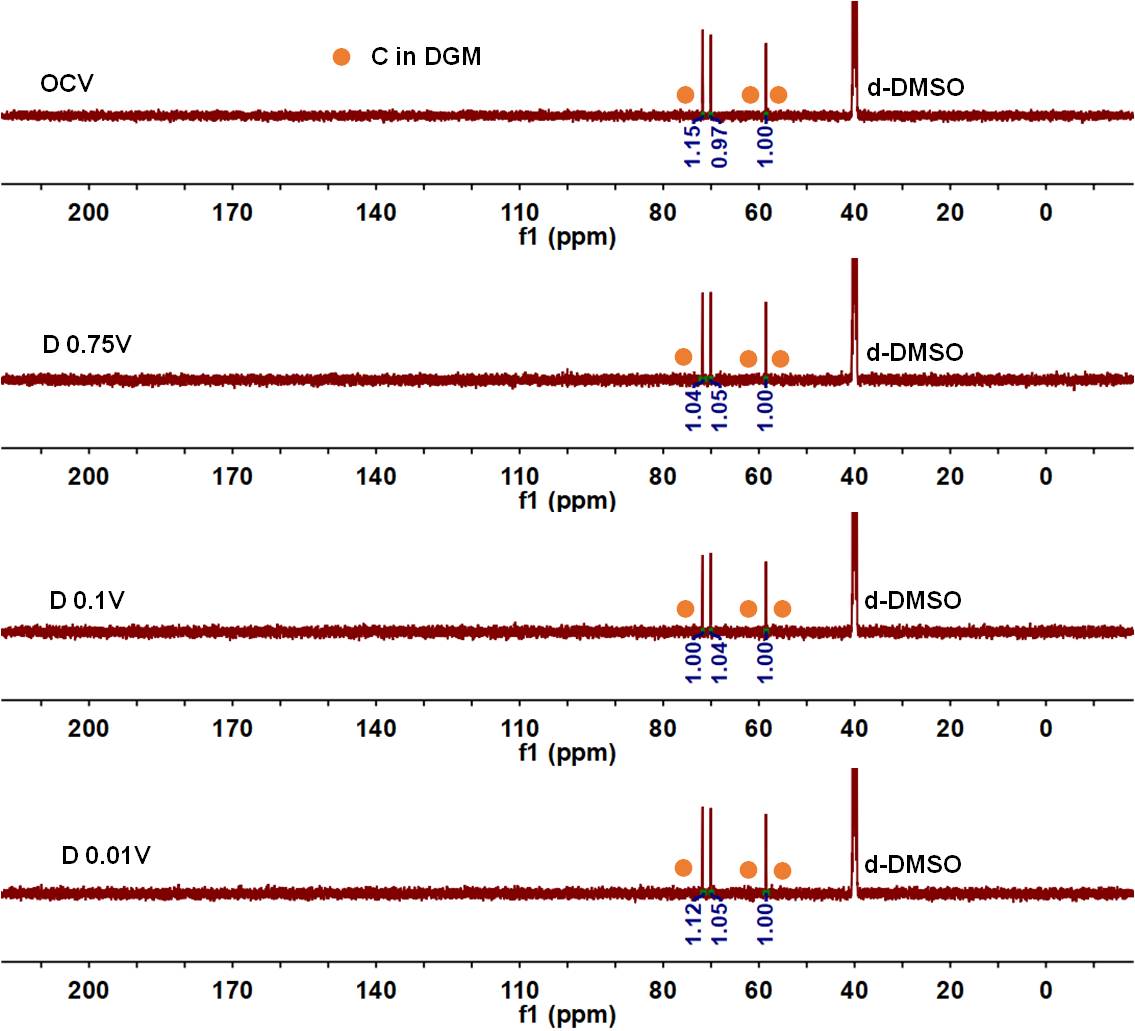
**Figure S3.** HRTEM images of hard carbon in DGM (a) and EC/DEC (b) at C1.5 V for the fifth cycle.



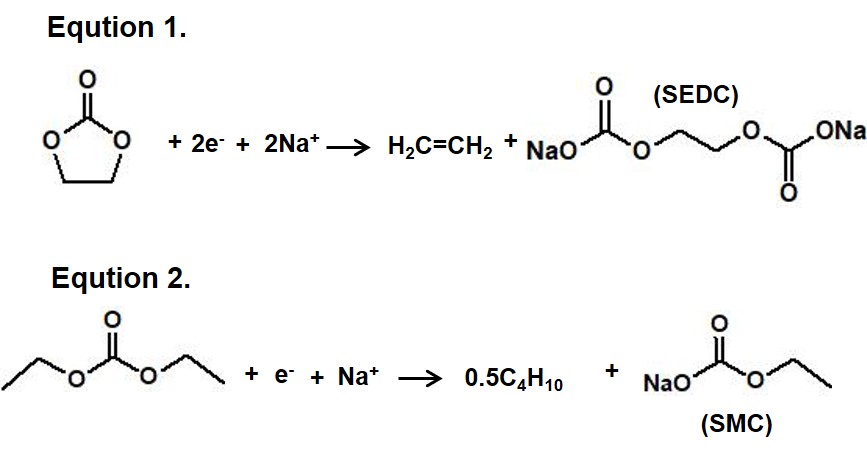
**Figure S4.** EIS spectra of hard carbon in DGM (a) and EC/DEC (b) at C1.5 V for the fifth cycle.



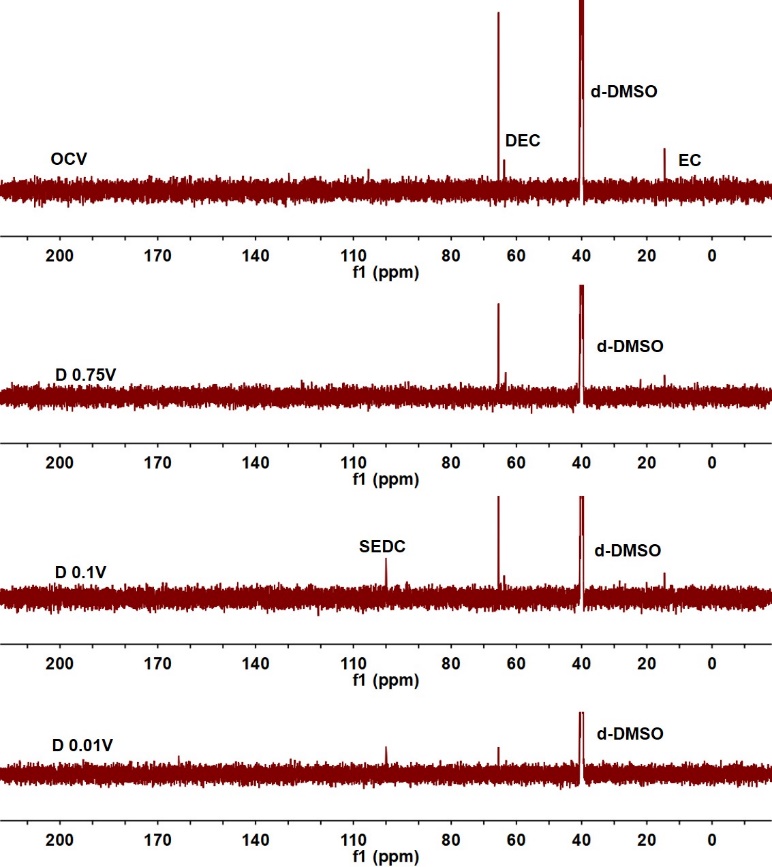
**Figure S5.** 1H NMR of pure electrolytes. (a) NaPF6 in DGM. (b) NaPF6 in EC/DEC.



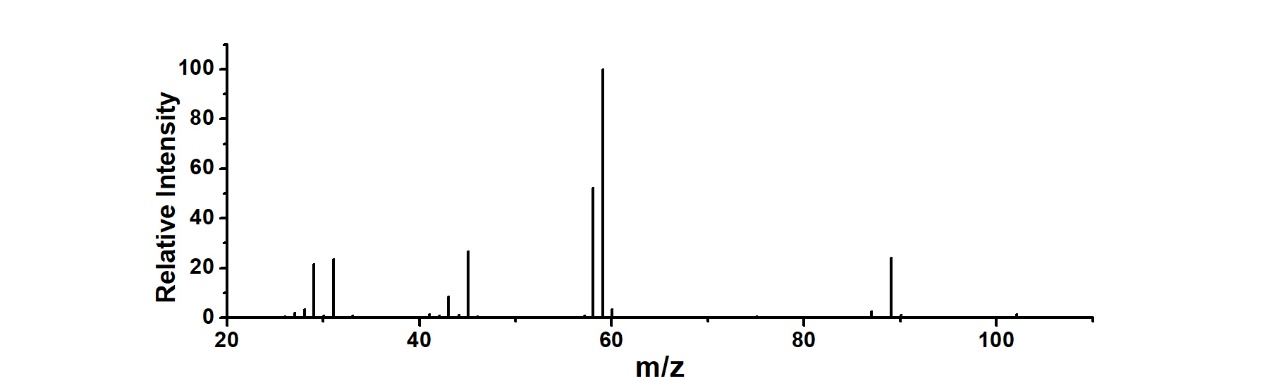
**Figure S6.** 13C NMR of NaPF6 in DGM.



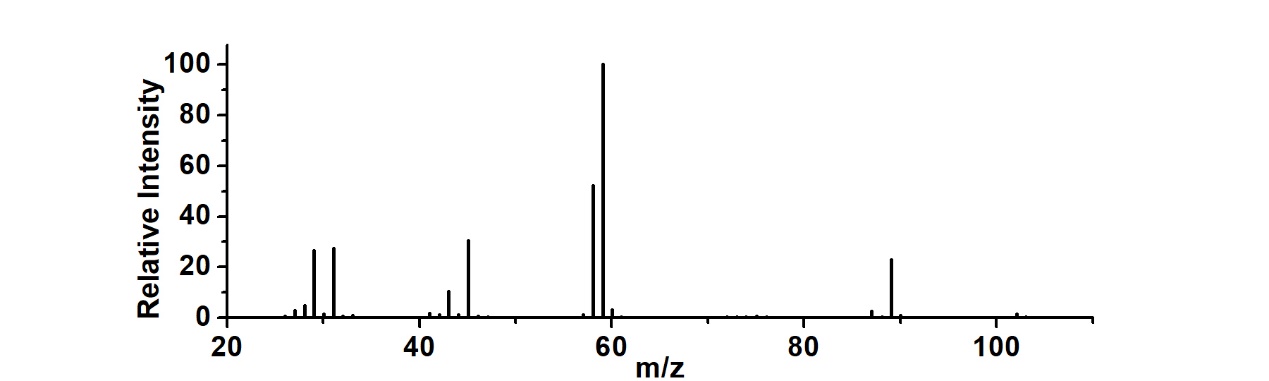
**Figure S7.** Equtions of EC and DEC reacted with Na+ during discharge process.



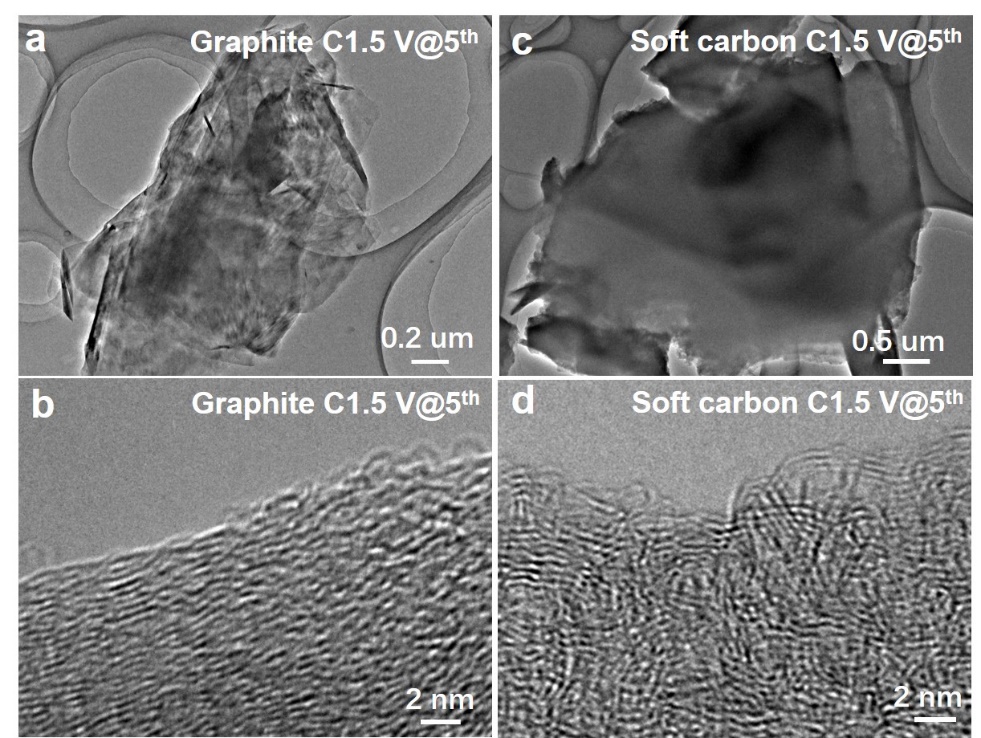
**Figure S8.** 13C NMR of NaPF6 in EC/DEC.

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**Figure S9.** Standard spectrum of MS of DGM in chloroform.

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**Figure S10.** MS of NaPF6 in DGM discharged to 0.01 V for the third cycle.



**Figure S11.** TEM andHRTEM images of carbon materials at C 1.5 V@5th in DGM. (a,b) Graphite. (c,d) Soft carbon..

**Table S1.** The sodium-storage properties of reported hard carbon anodes.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Hard carbon anode | Capacity  [mA h g-1] | Cycle life | | Capacity retention [%] | Ref. |
| LHC\_opc | 205 at 0.2 A g-1 | | 500 | 100 | 1 |
| RSS-700 | 143 at 0.1 A g-1 | | 200 | 72 | 2 |
| OPDHC-A | 210 at 2.0 A g-1 | | 3000 | 99 | 3 |
| HCNPs | 207 at 0.05 A g-1 | | 500 | 77 | 4 |
| LS1400 | 330 at 0.1 A g-1 | | 450 | 91.6 | 5 |
| RPC-600 | 135 at 0.1A g-1 | | 1000 | 90 | 6 |
| LJ-1300 | 288 at 0.1 A g-1 | | 200 | 91.8 | 7 |
| CPP | 203 at 0.1 A g-1 | | 200 | 98 | 8 |
| CP | 131.5 at 0.5 A g-1 | | 500 | 89.8 | 9 |
| SGHC-1000 | 136 at 1 A g-1 | | 1000 | 86 | 10 |
| HC | 180 at 0.1 A g-1 | | 500 | 95 | 11 |
| HC | 70 at 0.2 A g-1 | | 1500 | 84 | 12 |
| HC | 196 at 1 A g-1 | | 2000 | 90 | 13 |
| HC | 200 at 0.5 A g-1 | | 1000 | 100 | 14 |
| CEM-G-8h | 140 at 0.5 A g-1 | | 2000 | 98 | 15 |
| S-HC | 323 at 0.02 A g-1 | | 200 | 98 | 16 |
| HC-P15 | 386 at 0.02 A g-1 | | 100 | 98.2 | 17 |
| MV-HC | 150 at 0.2 A g-1 | | 1100 | 85 | 18 |
| CNB | 128 at 0.5 A g-1 | | 1000 | 68 | 19 |
| Hard carbon | 224.4 at 1.0 A g-1 | | 3500 | 88 | Ours |

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