

Electronic Supplementary Information for Energy & Environmental Science

Electronic Supplementary Information

Dual-Graphite Chemistry Enabled by High Voltage Electrolyte

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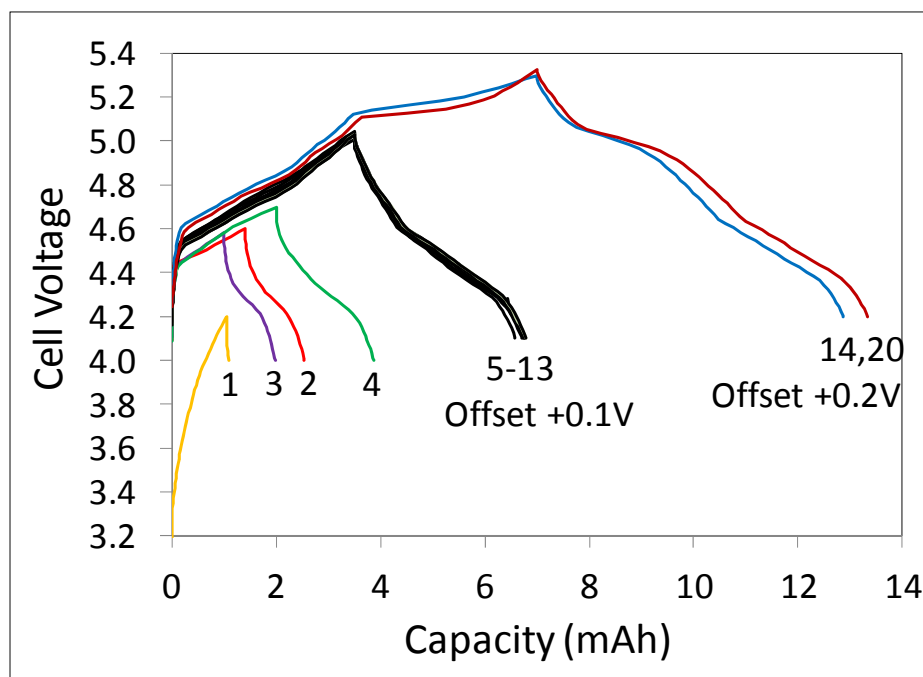


Figure S1. Initial cycling of cell from Figure 2. Cycle numbers 1-20 are shown with cycles 5-13 shifted up in voltage by +0.1V and cycles 14 and 20 shifted up in voltage by +0.2V. Cycling is at 0.5mA with the formation cycles (1-13) controlled as follows:

Cycle 1	Charge to 4.2V	Discharge to 4V
Cycle 2	Charge to 4.6V	Discharge to 4V
Cycle 3	Charge to 1.0 mAh	Discharge to 4V
Cycle 4	Charge to 2.0 mAh	Discharge to 4V
Cycle 5-13	Charge to 3.5 mAh	Discharge to 4V
Cycle 14-200+	Charge to 7.0 mAh	Discharge to 4V

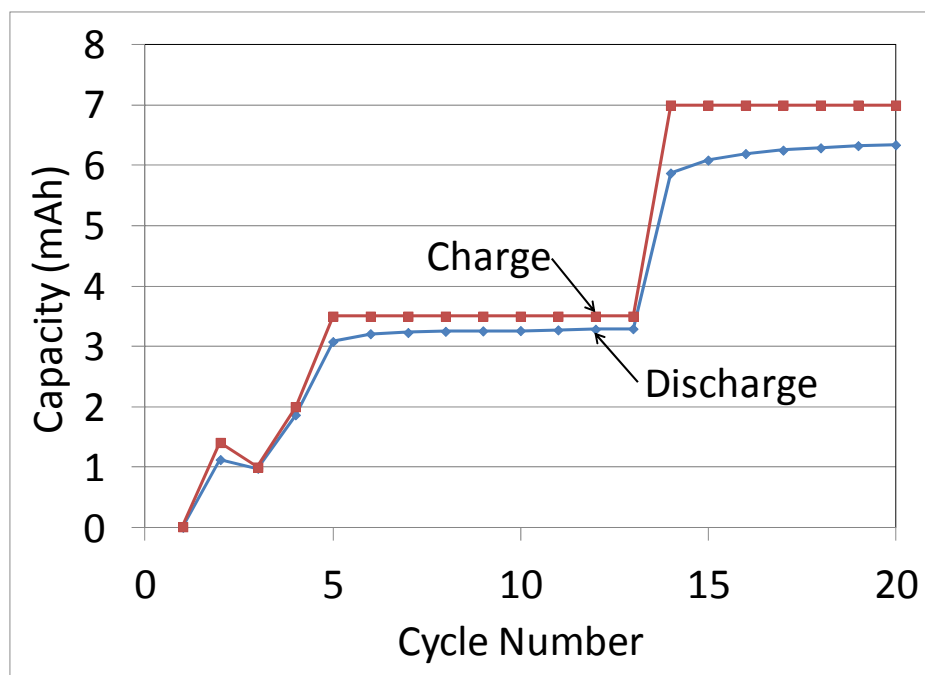


Figure S2. Initial charge and discharge capacities of cell from Figure 2.

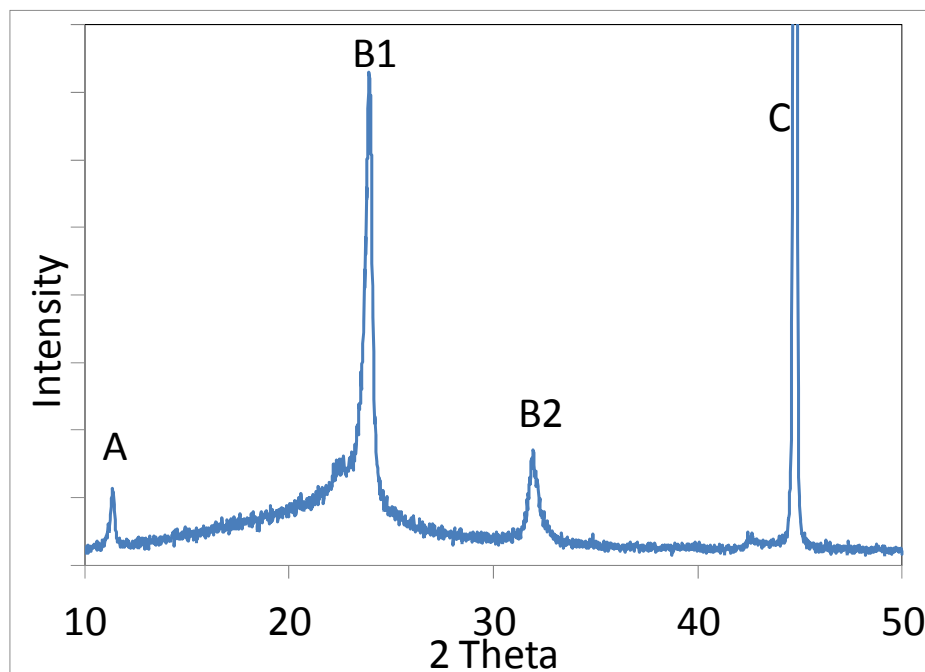


Figure S3. XRD on fully charged MCMC 10-28 cathode. (A) Stage 1 Interlate ($11.36^\circ 2\theta$, $d_{001} = 7.783 \text{ \AA}$) (B1) Stage 3 intercalate ($23.92^\circ 2\theta$, $d_{003} = 3.717 \text{ \AA}$) (B2) Stage 3 intercalate ($31.94^\circ 2\theta$, $d_{004} = 2.800 \text{ \AA}$) and (C) Aluminum current collector.

Cycled electrodes were removed from cells in the dryroom and examined by XRD. XRD measurements were taken at $2^\circ 2\theta$ per minute between 10° and $50^\circ 2\theta$ on a Rigaku Ultima III using $\text{Cu K}\alpha$ radiation in Bragg-Brentano configuration. Peaks B2 and B3 were used to calculate stage number n from Equation 6 in reference 6. The PF_6 gallery height calculated using the stage 1 and stage 3 values is $4.423 \text{ \AA}$ to $4.429 \text{ \AA}$ respectively, similar to values in reference 6.

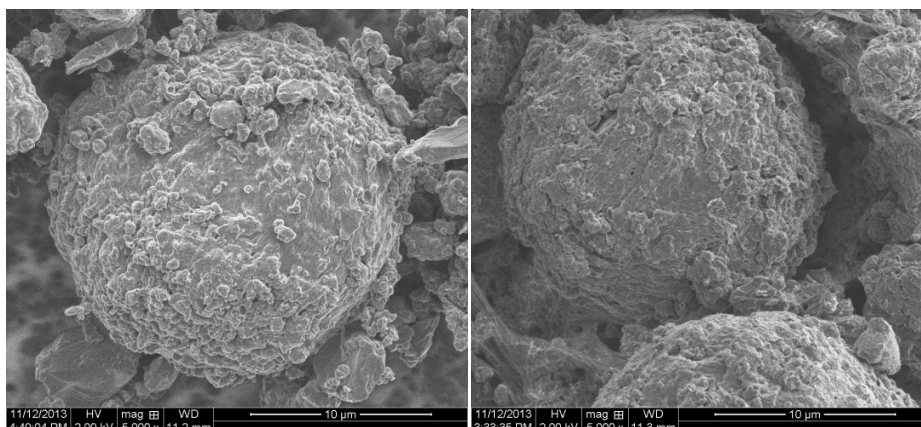


Figure S4. (A) Uncycled MCMB 10-28 graphite powder and (B) Cycled MCMB 10-28 graphite electrode.

SEM Images were taken on a FEI Environmental SEM.

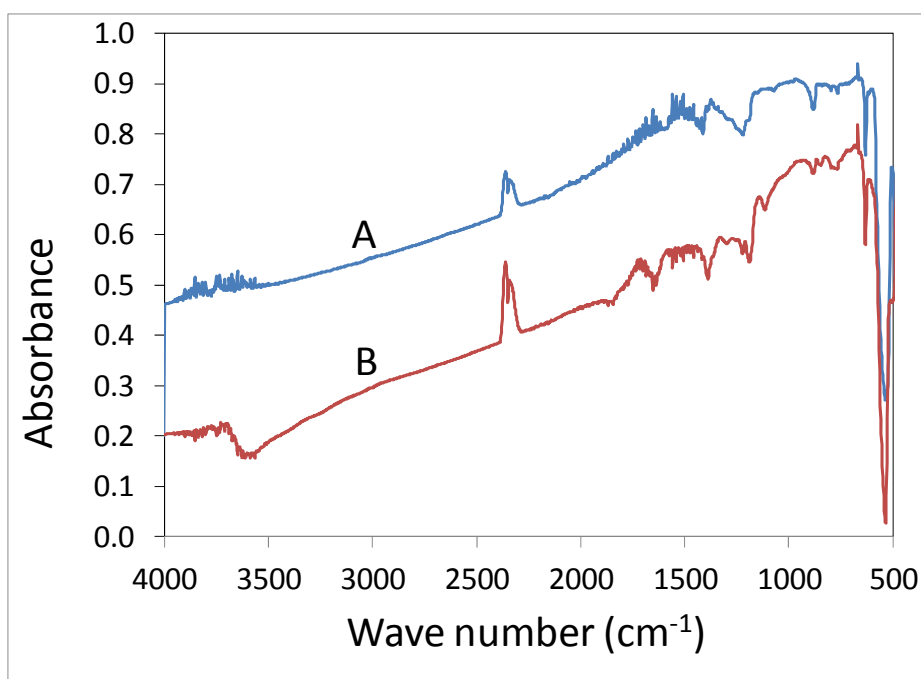


Figure S5. (A) Uncycled MCMB 10-28 graphite electrode and (B) Cycled MCMB 10-28 graphite electrode. Uncycled electrode shifted up by 0.2 absorbance units for clarity.

Spectra were taken after electrode extraction in dimethyl carbonate on a Nicolet 6700 FTIR using an Attenuated total reflectance (ATR) crystal cell designed for air sensitive samples.

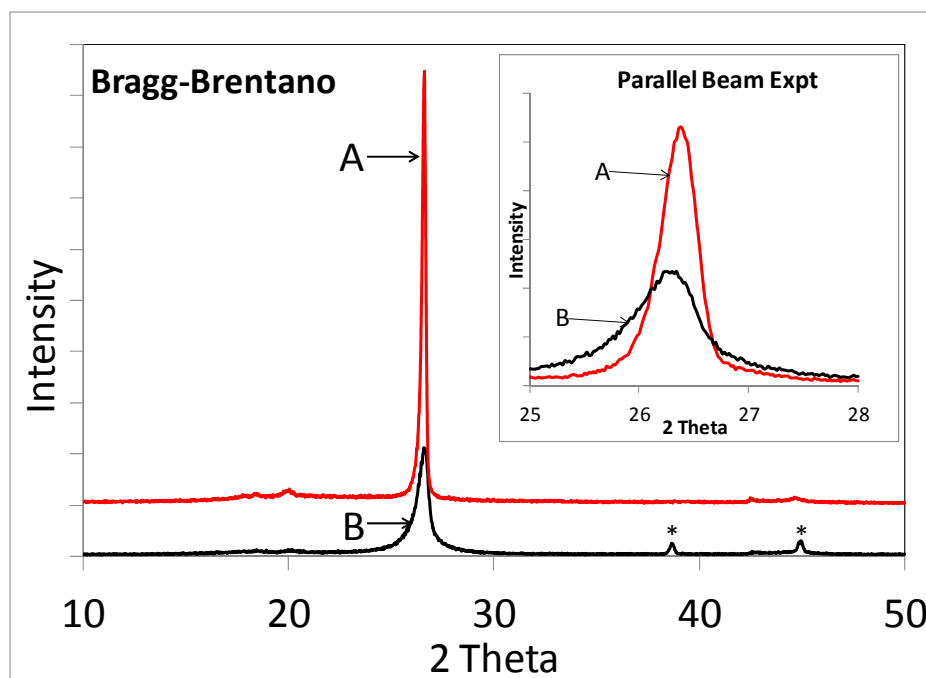


Figure S6. Bragg-Brentano XRD to determine crystallite size and Parallel Beam XRD for peak position of
(A) Uncycled electrode ($d_{002} = 3.361\text{\AA}$, crystallite size = $480\text{\AA}$)
(B) Cycled and discharged cathode ($d_{002} = 3.374\text{\AA}$, crystallite size = $110\text{\AA}$)
* Aluminum current collector

Cycled electrodes were washed in dimethyl carbonate and dried before being examined by XRD. XRD measurements were taken at $2^\circ 2\Theta$ per minute between 10 and $50^\circ 2\Theta$ on a Rigaku Ultima III using $\text{Cu K}\alpha$ radiation in either Bragg-Brentano or parallel beam configuration. Peak positions in parallel beam mode were determined using NIST Standard Reference Material 640c Silicon powder. Crystallite size was determined from the Bragg-Brentano XRD spectra using the Jade 7 Pattern Processing, Identification, and Quantification software program. Peaks were fit using the pseudo-Voigt function with crystallite size calculated using the Scherrer equation.

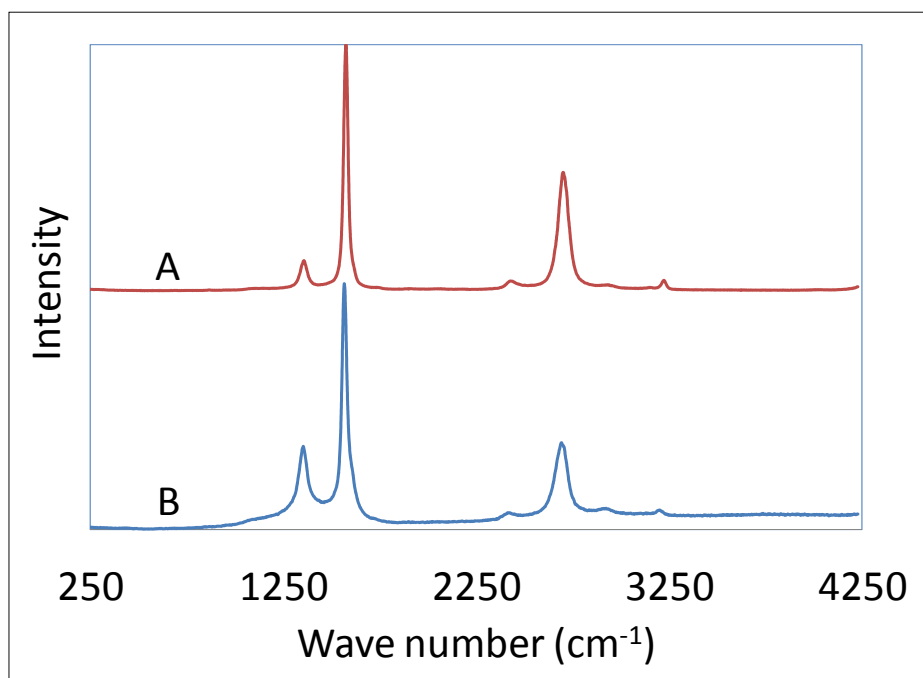


Figure S7. (A) Uncycled MCMB 10-28 graphite powder and (B) Cycled MCMB 10-28 graphite electrode. Uncycled curve shifted up by for clarity.

Spectra were taken after electrode extraction in dimethyl carbonate in air on a Witec alpha 300 RA scanning Raman microscope using a 50x objective, averaging 60 x 1 second acquisitions, with 1 mW laser power, from a 488 nm laser.

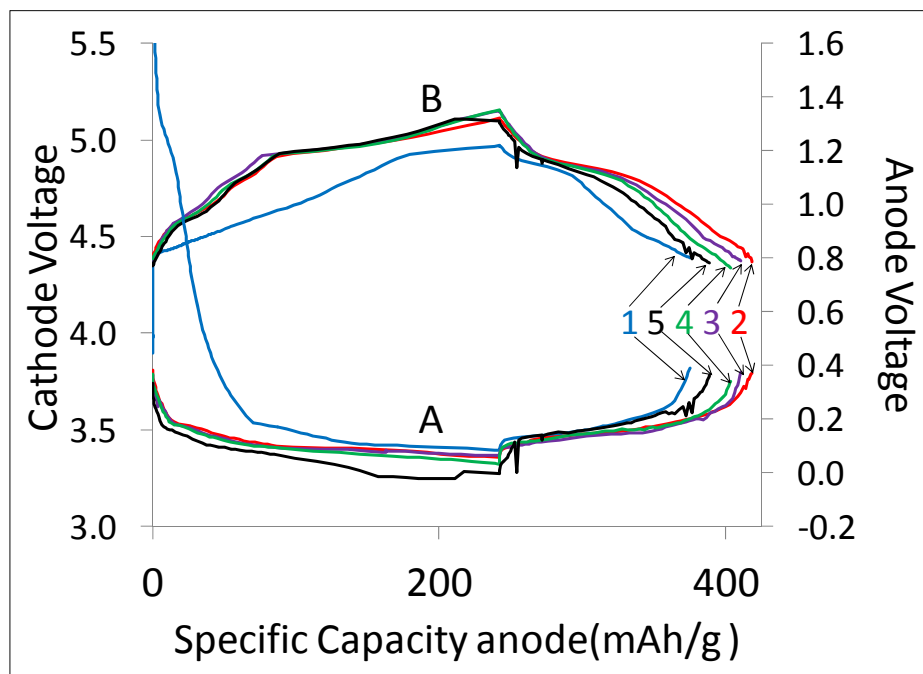


Figure S8. Full dual-graphite pouch cell with Li reference electrode cycled at C/20 with capacity normalized to graphite anode. Cycles 1-5 of (A) CGP-G5 anode and (B) MCMB 10-28 cathode.

2035 Coin Cell Preparation

MCMB 10-28 graphite from Osaka Gas was used for the cathode graphite while CGP-G5 or CGP-A12 “CPreme” from Conoco Phillips was used for the anode graphite. CGP-A12 anodes were supplied on copper foil by Argonne National Labs.

MCMB 10-28 and CGP-G5 electrodes were prepared by mixing graphite, carbon black (Super P, M.M.M. Carbon), dibutylphthalate (DBP) plasticizer, vinylidene fluoride copolymer (Kynar 2801, Arkema) at weight ratios of 56:3:23:18 with acetone in a 500 ml stainless steel blender cup. The resulting slurry was cast on glass and dried in air. For use in coin cells, the plasticized films were extracted in methanol 3 times to remove the DBP and dried under vacuum at 105°C for 1 hour before cell assembly. Cells were constructed in a dryroom or drybox using 2035 coin cell hardware (Hoshen).

Aluminum clad cathode cans and stainless steel anode cans were used for half cell cathode and full cell cycling while half cell anode cycling was carried out using stainless steel cans for both cell halves. The aluminum clad cathode cans were prepared for high voltage cycling by coating the inside of the can with a Super P/ polyethylene acrylic acid based primer (MICA D-709) in a 1:1 by weight ratio or by ultrasonically welding a Pt foil to the inside of the can where it contacted the cathode electrode. The carbon black coating or Pt foil reduced the buildup of contact resistance that would result in random cell failure after 40-60 cycles in 2035 coin cells.

Cells were assembled using anode (0.020” lithium foil or CGP-A12 on copper) , 2 layers of Celgard 3401 or 2400 separator, one on either side of a non-woven polypropylene separator, and electrolyte. Cell impedance and OCV were measured for each cell before being placed on test. All cells were cycled on a Maccor Series 4000 cyclers.

Laminated Pouch Cell Preparation

5 cm² electrodes were cut from the plasticized cathode films and then laminated to aluminum grids that were pre treated with a Super P/ polyethylene acrylic acid based primer to insure good contact. Plasticized anode films were laminated to copper grids pre treated with the same primer mixture. For half cell construction, the cathode after lamination was tabbed then extracted in methanol 3 times to remove the plasticizer, DBP. Electrodes were dried under vacuum at 105°C for 1 hour before cell assembly. Cells were constructed in a dryroom from 0.020” lithium foil pressed onto a tabbed nickel grid, 2 layers of Celgard 3401 separator on either side of a layer of non woven polypropylene separator, and the laminated cathode. The cell was held together by two polypropylene blocks bound with coated wires. The assembled half cell stack was then placed in a foil pouch and sealed. Electrolyte was added in excess and the cell was vacuum sealed. Cell impedance and OCV were measured for each cell before being placed on test. All cells were cycled on a Maccor Series 4000 cyclers at C/5-C/15 rates.

For full cell construction, the laminated anode and cathode were laminated together using a plasticized separator composed of 33.3% Kynar 2801, 22.2% fumed silica (TS-530, Cabot), and 44.4% DBP. The laminated cell was then extracted 3 times in methanol and dried under vacuum at 105C for a minimum of 1 hour. The cell was then placed in a foil pouch, electrolyte was added, and the cell was sealed under vacuum.

3 and 4 electrode studies

3 electrode pouch cells were built with lithium reference electrodes to monitor anode and cathode potential upon cycling in full laminated cells. Graphite-Li half cells were built with a Platinum-Li cell inserted at the edge of the separator to create a four electrode cell in order to investigate the presence of soluble electroactive species in the electrolyte. The Graphite-Li half cell was cycled on a MACCOR Series 4000 cyclers while the Platinum-Li cell was cycled on a Solartron 1260/1287.