# Supplementary Information

### **Durable Potassium Ion Battery Electrodes from High-Rate**

## **Cointercalation into Graphitic Carbons**

Adam P. Cohn<sup>1</sup>, Nitin Muralidharan<sup>2</sup>, Rachel Carter<sup>1</sup>, Keith Share<sup>2</sup>, Landon Oakes<sup>2</sup>, and Cary L.

 $Pint^{1,2}*$ 

<sup>1</sup>Department of Mechanical Engineering, Vanderbilt University, Nashville, TN 37235 <sup>2</sup>Interdisciplinary Materials Science Program, Vanderbilt University, Nashville, TN 37235

\* Corresponding Author, electronic mail: <u>cary.l.pint@vanderbilt.edu</u>

#### Supplementary video:

**Video S1:** Video showing the vibrant color changes in the graphene foam that coincide with the cointercalation reaction during cyclic voltammetry testing of MLG foam/ 1 M KPF<sub>6</sub> DGM/ K metal half cells at a scan rate of 5 mV/s. The video is presented at 30x the original speed. The transition to black during insertion corresponds to the stage 2 formation and then the subsequent transition to red/orange corresponds to the stage 1 formation. We attribute the color change to the increased electron concentration in the graphene layers and a resulting Pauli blocking effect. The video was captured using the *in-situ* test cell used for Raman and an optical microscope with a L50x objective. The scale bar is 20  $\mu$ m. Video S1 is available on the publisher's website.

#### **Experimental Details**

#### **Electrode synthesis**

MLG foam electrodes were grown on Ni foam templates (MTI, 110 ppi) using CVD processes in a tube furnace. The foam was heated to 850 °C under flows of Ar and H<sub>2</sub> and annealed for 20 minutes,  $C_2H_2$  was introduced with respective flow rates of C2H2:H2:Ar at 1:3:500 sccm for 60 minutes and then the  $C_2H_2$  flow was halted and the system was cooled to room temperature. Afterwards, the Ni was removed using HCl dissolution. Then the MLG foam was repeatedly rinsed in DI water prior to use.

#### **Electrochemical testing**

Natural graphite (Alfa Aesar) was mixed with polyvinylidene fluoride (MTI) and carbon black (C45, MTI) using a ratio of 90:7:3 in N-Methyl-2-pyrrolidone solvent prior to being cast on Cu foil disks to obtain active mass loading of ~1 mg/cm<sup>2</sup>. MLG foam electrodes were dried (from DI water bath) on Cu foil disks with active mass loading of ~0.2 mg/cm<sup>2</sup>. Working electrodes were tested using 2032 coin cells (MTI) assembled in an Ar glovebox using a K metal counter/reference electrode (99.5%, Sigma-Aldrich) a Whatman grade GF/F glass fiber microfiber filter separator (Sigma Aldrich) and an electrolyte of 1M KPF6 (99.5%, Sigma-Aldrich). Galvanostatic measurements were performed using either a MTI 8 channel battery analyzer or Metrohm Autolab multichannel electrochemical workstation. Extended cycling data was performed after initial device characterization (~50 cycles).

#### Material characterization

X-ray diffraction measurements were conducted using a using a Scintag XGEN 4000 system with a CuK $\alpha$  radiation source. Raman measurements were conducted using a Renishaw inVia Raman spectrometer with a 532 nm laser. SEM and EDS characterization was performed using a Zeiss MERLIN with GEMINI II SEM. To characterize the charged state, an airtight cell with a Be window was used for performing XRD measurements and a homemade airtight cell with a coverslip window was used for performing Raman measurements. To characterize the postcycled material, coin cells were disassembled in the glovebox and the working electrodes were removed and rinsed in diglyme and dried under vacuum prior to performing measurements.

#### In-situ Raman spectroscopy

*In-situ* measurements were conducted through a coverslip window in an airtight chamber containing an assembled coin cell with a small hole to reveal the MLG foam. The potential of the cell was controlled using a single-channel Metrohm Autolab. A linear sweep rate of 0.5 mV/s was used and Raman scans were acquired over 30s intervals using an L50x objective, a 532 nm laser, a ~1.5  $\mu$ m spot size, and ~600 mW laser power. The MLG was left on the Ni support for testing. Spectra fits were performed using Lorentzian curves.



Figure S1. Initial cycling performed at 0.2 A/g for graphite half cells with 1M KPF<sub>6</sub>. Initial irreversible capacity is attributed to the reduction of the electrolyte.



Figure S2. Galvanostatic charge-discharge profiles for the first 5 cycles performed at 0.2 A/g using diglyme solvent.



Figure S3. Galvanostatic charge-discharge profiles for the first 5 cycles performed at 0.2 A/g using monoglyme solvent.



Figure S4. EDS spectrum of the intercalated MLG foam (corresponding to Fig. 2 E,F in the main text).



Figure S5. Galvanostatic Intermittent Titration Technique (GITT). GITT profile shows that the MLG electrode operates near equilibrium conditions during charging and discharging, indicating short diffusion times. Measurements were performed using 60 second pulses followed by 300 second rests. After stage 1 was reached (below 0.8V), essentially no change in potential was observed to occur during the rest periods which may be due to supercapacitor-like behavior when ions and solvent are in-between all graphene sheets.



Figure S6. In-situ Raman analysis of the evolving G peak double with the component peak position plotted with respect to cell potential. The corresponding measured current during the linear voltage sweep is shown on the right.



Figure S7. In-situ Raman acquired during the second insertion. Initial spot shows small G<sub>C</sub> component in the uncharged state, possibly indicating remnant K ions.