SUPPORTING INFORMATION

Elucidating the Sodiation Mechanism in Hard Carbon by Operando Raman Spectroscopy

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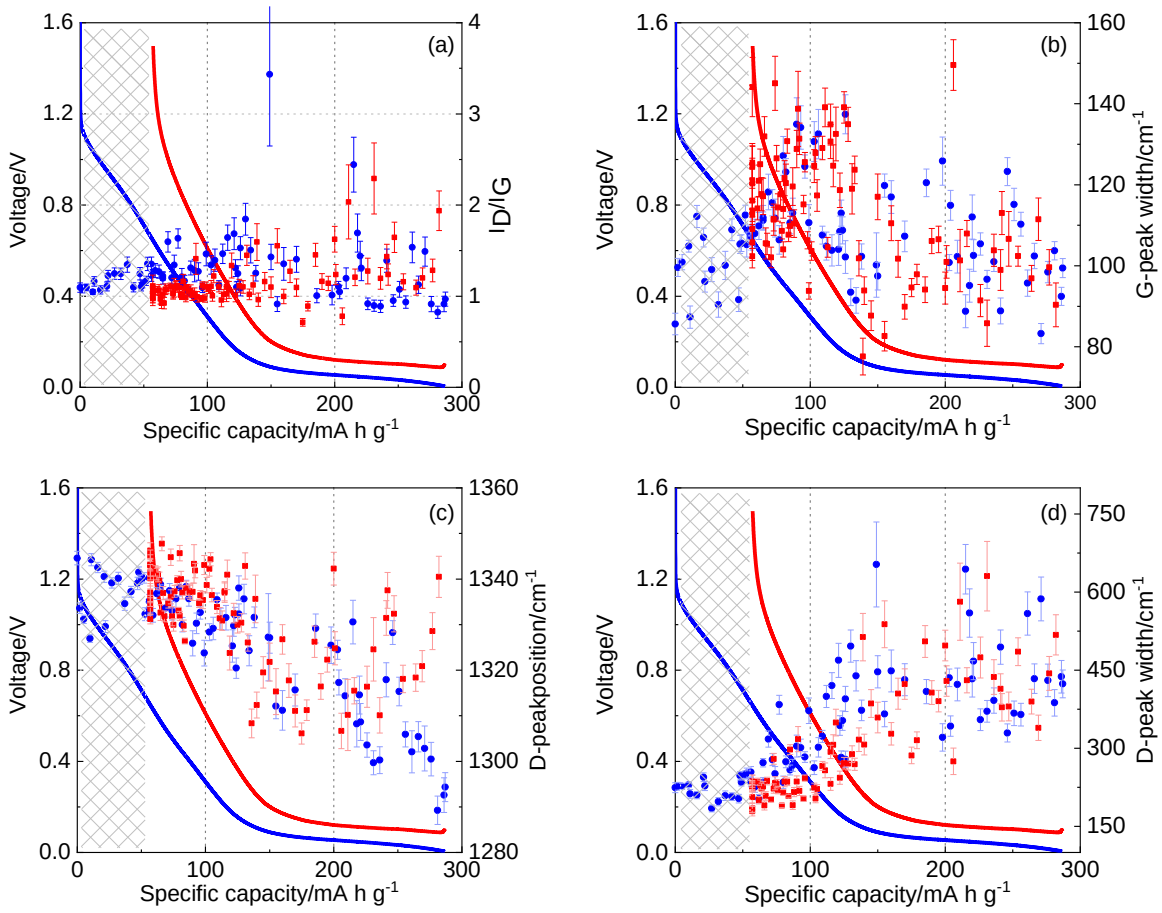

Figure S1 Operando Raman experiment for discharge (sodiation) and subsequent charge (desodiation) on cycle-1 of sodium-hard carbon cell described in Figure 3; sodiation shown in blue; desodiation shown in red; solid line = voltage profile, discrete points = Raman parameters from fitted G- and D-peaks (blue dots =sodiation, red squares = desodiation): (a) ratio of intensities I_D/I_G; (b) G-peak width, (c) D-peak position, (d) D-peak width; First Cycle Loss associated with SEI formation shown in grey shading; sodiation was carried out by discharging at constant current of C/5 to 5 mV (there was no constant voltage hold) and desodiation was at a constant current charge of C/5 to 1.5 V; C/5 was based on 300 mA h g^{-1} for hard carbon; G-peak position given in Figure 3.

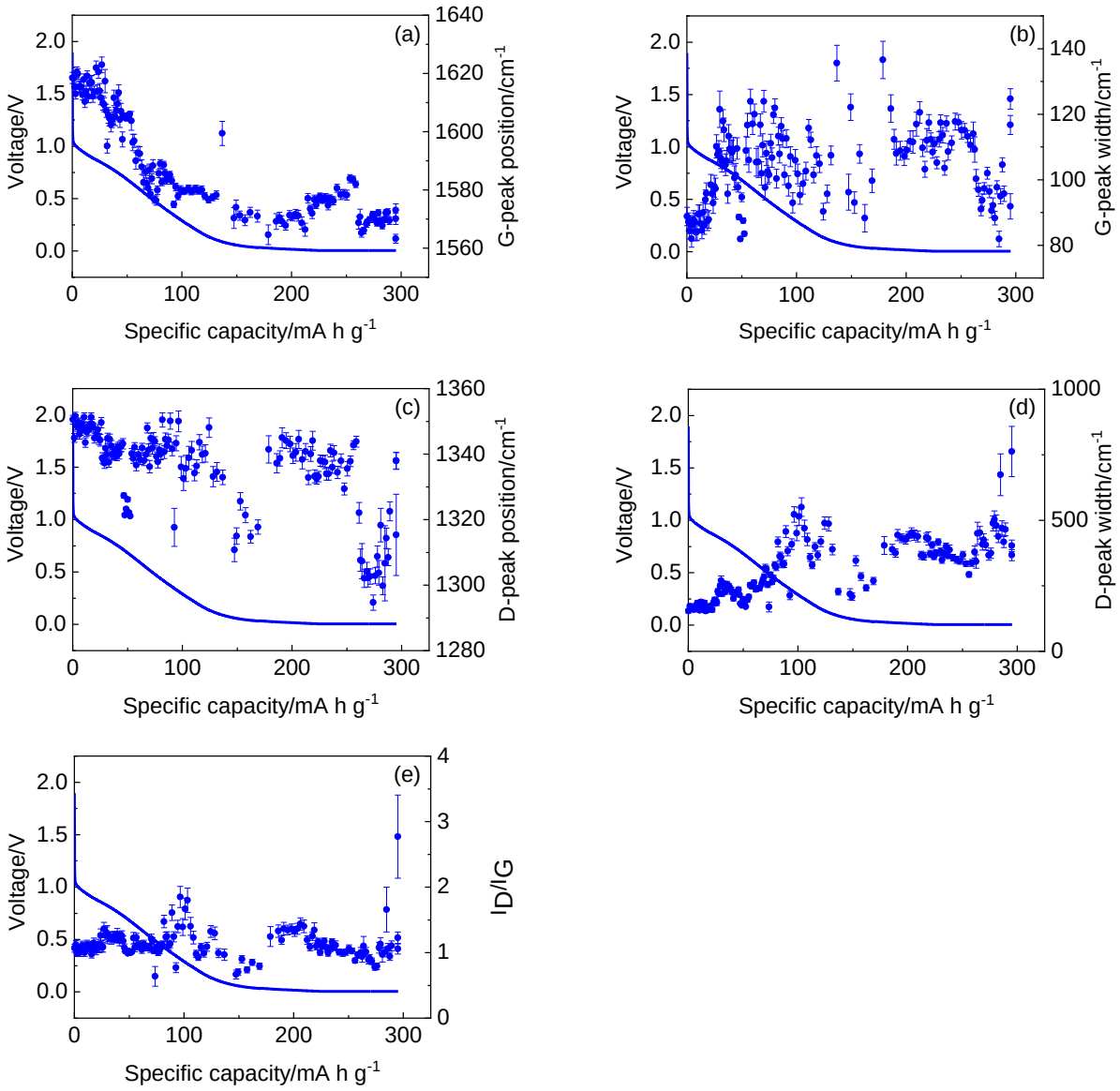

Figure S2 Operando Raman experiment for discharge (sodiation) of sodium-hard carbon cell on cycle-1; solid line = voltage profile, discrete points = Raman parameters from fitted G- and D-peaks: (a) G-peak position; (b) G-peak width; (c) D-peak position; (d) D-peak width; (e) ratio of intensities I_D/I_G; sodiation was carried out by discharging at constant current of C/3 to 5 mV, followed by a constant voltage hold at 5 mV for 60 minutes; C/3 was based on 300 mA h g^{-1} for hard carbon.

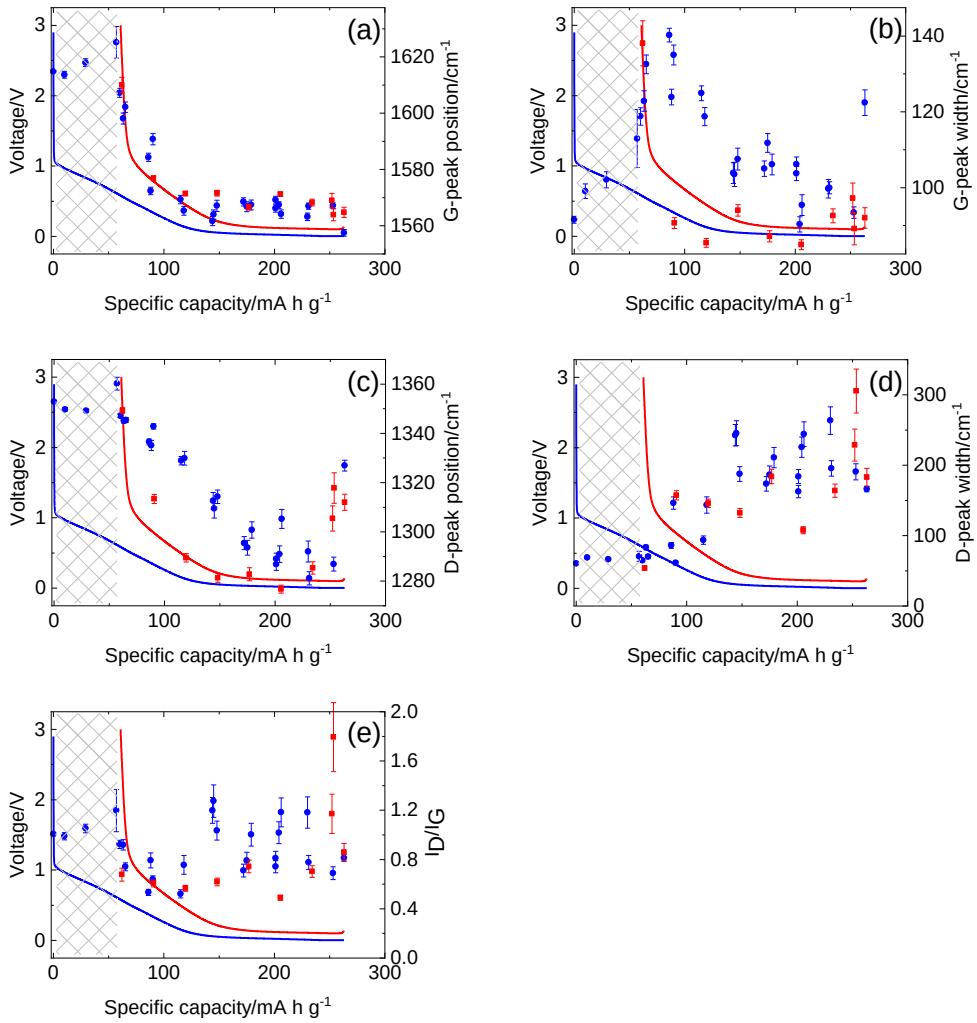

Figure S3 Operando Raman experiment for discharge (sodiation) and subsequent charge (desodiation) of sodium-hard carbon cell on cycle-1; sodiation shown in blue; desodiation shown in red; First Cycle Loss associated with SEI formation shown in grey shading; solid line = voltage profile, discrete points = Raman parameters from fitted G- and D-peaks (blue dots =sodiation, red squares = desodiation): (a) G-peak position, (b) G-peak width, (c) D-peak position, (d) D-peak width and (e) ratio of intensities I_D/I_G; sodiation was carried out by discharging at constant current of C/5 to 5 mV, followed by a constant voltage hold at 5 mV for 30 minutes; desodiation was at a constant current charge at C/5 to 3 V; C/5 was based on 300 mA h g^{-1} for hard carbon.

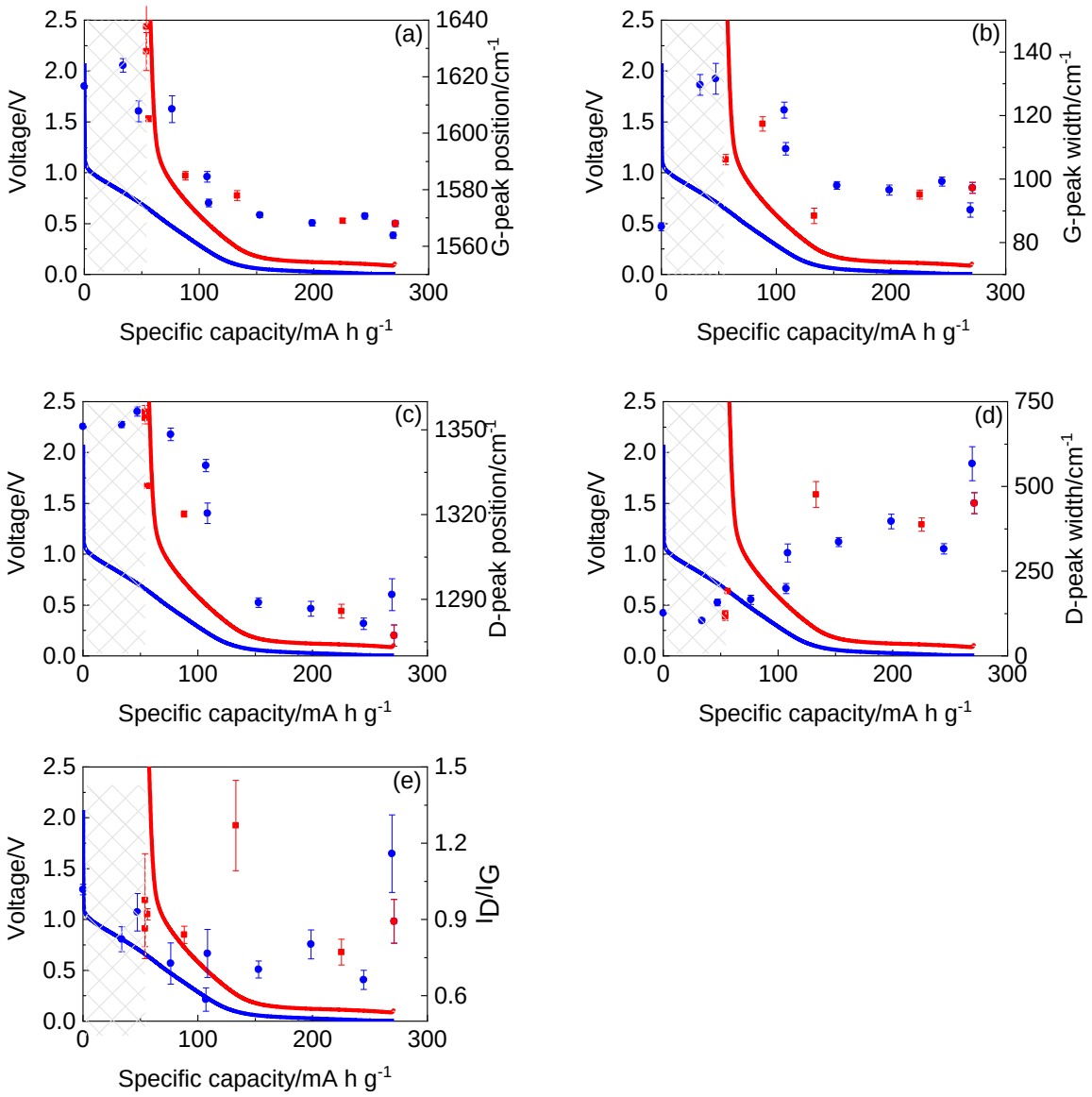

Figure S4 Operando Raman experiment for discharge (sodiation) and subsequent charge (desodiation) of sodium-hard carbon cell on cycle-1; sodiation shown in blue; desodiation shown in red; First Cycle Loss associated with SEI formation shown in grey shading; solid line = voltage profile, discrete points = Raman parameters from fitted G- and D-peaks (blue dots =sodiation, red squares = desodiation): (a) G-peak position, (b) G-peak width, (c) D-peak position, (d) D-peak width and (e) ratio of intensities I_D/I_G; sodiation was carried out by discharging at constant current of C/3 to 5 mV, followed by a constant voltage hold at 5 mV for 17 minutes; desodiation was at a constant current charge at C/3 to 3.5 V; C/3 was based on 300 mA h g^{-1} for hard carbon.

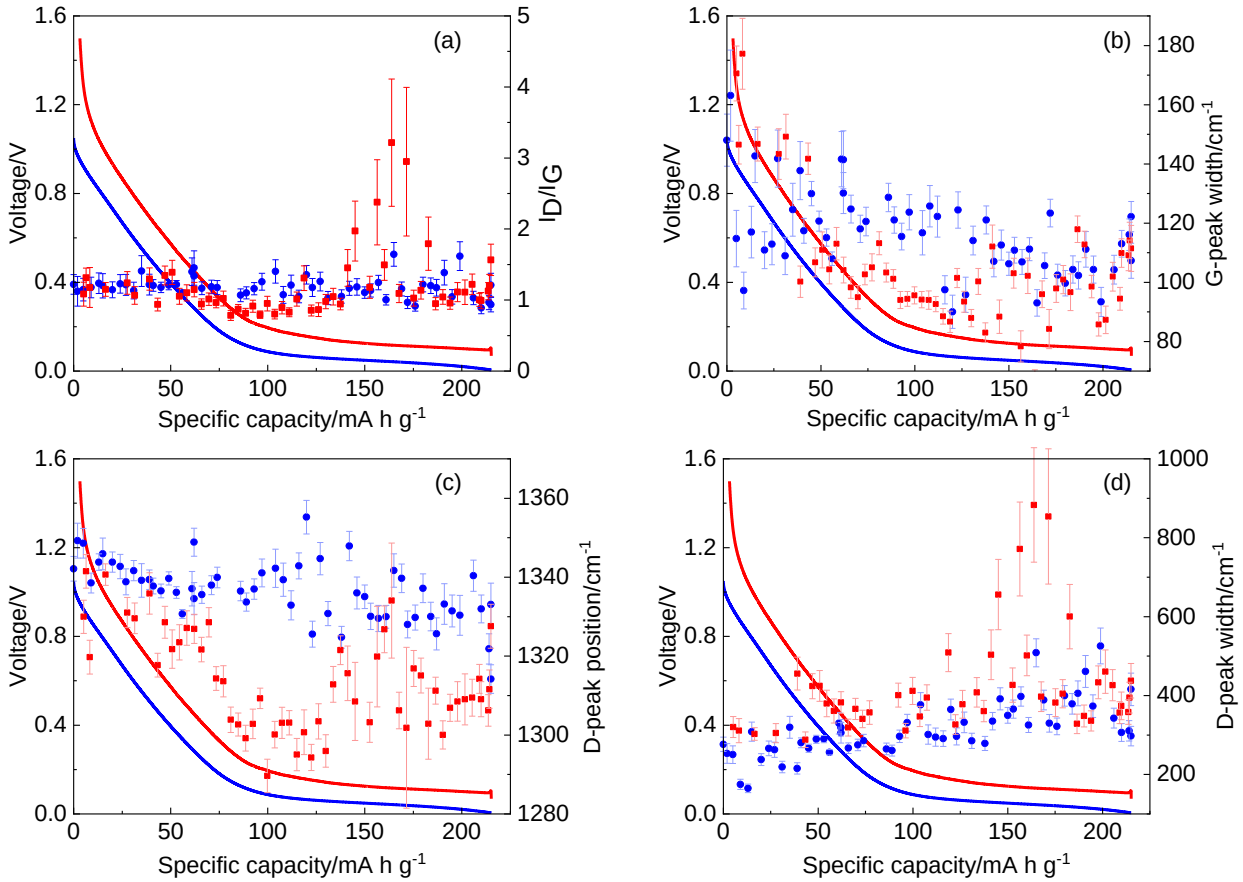

Figure S5 Operando Raman experiment for discharge (sodiation) and subsequent charge (desodiation) on cycle-9 of sodium-hard carbon cell described in Figure 3 and Figure S1; sodiation shown in blue; desodiation shown in red; solid line = voltage profile, discrete points = Raman parameters from fitted G- and D-peaks (blue dots =sodiation, red squares = desodiation): (a) ratio of intensities I_D/I_G; (b) G-peak width; (c) D-peak position; (d) D-peak width; sodiation was carried out by discharging at constant current of C/5 to 5 mV (there was no constant voltage hold) and desodiation was at a constant current charge at C/5 to 1.5 V; C/5 was based on cycle-1 charge (desodiation) capacity (Figure 3 and Figure S1); G-peak position given in Figure 3.

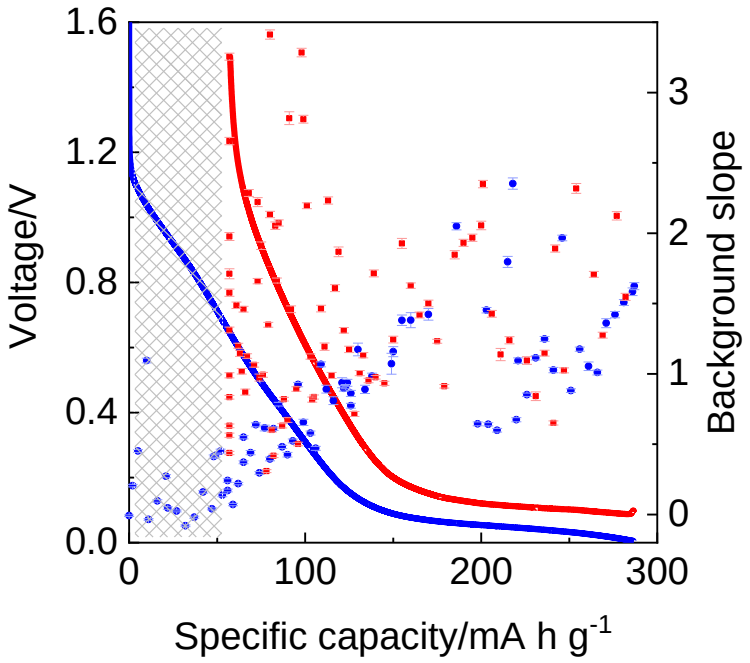

Figure S6 Background slope plotted with voltage profile against specific capacity for Raman spectra recorded during discharge (sodiation) and subsequent charge (desodiation) on cycle-1 of sodium-hard carbon cell described in Figure 3; sodiation shown in blue; desodiation shown in red; solid line = voltage profile, discrete points = background slope (blue dots =sodiation, red squares = desodiation); First Cycle Loss associated with SEI formation shown in grey shading.

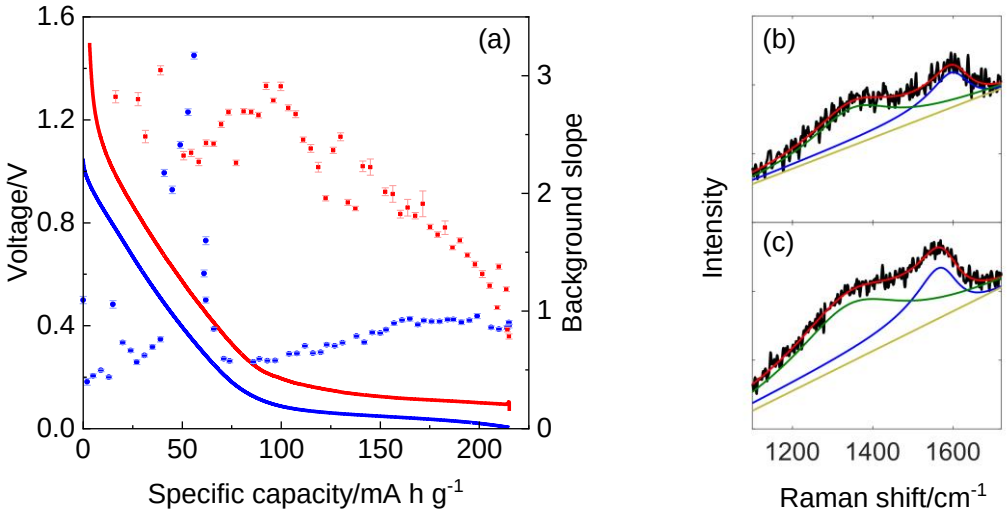

Figure S7 (a) Background slope plotted with voltage profile against specific capacity for Raman spectra recorded during discharge (sodiation) and subsequent charge (desodiation) on cycle-9 of sodium-hard carbon cell described in Figure 3; sodiation shown in blue; desodiation shown in red; solid line = voltage profile, discrete points = background slope (blue dots = sodiation, red squares = desodiation); (b)-(c) selected spectra recorded at different capacities during sodiation on cycle-9: (b) 5 mA h g^{-1}, (c) 97 mA h g^{-1}; data (black), total fit (red), Lorentzian fit (green), Breit-Wigner-Fano fit (blue), background (dark yellow).