A novel elevated temperature pre-treatment for electrochemical capacity enhancement of graphene nanoflake-based anodes

Sandeep Bhattacharya¹ · Ahmet T. Alpas¹

Received: 22 November 2017 / Accepted: 2 February 2018 / Published online: 16 February 2018
© The Author(s) 2018. This article is an open access publication

Abstract

Improvements in the specific capacity of graphene nanoflake-based anodes cycled vs. Li/Li^+ were investigated at two cycling temperatures of 25 and 50 °C. When cycled at 25 °C, the first cycle specific capacity of the graphene nanoflakes was 636 mA h g^{-1} , whereas cycling at 50 °C led to a 35% increase in the specific capacity to 856 mA h g^{-1} . High resolution SEM investigations revealed that the increased capacity of graphene cycled at 50 °C was accompanied by the formation of a uniform and continuous solid electrolyte interface (SEI). The strain generated in graphene anodes was reduced from 0.75% at 25 °C, to 0.12% at 50 °C, as determined by in situ Raman spectroscopy. This was attributed to the reduction in the extent of solvent co-intercalation at 50 °C. The results suggest that pre-cycling of Li-ion cell anodes containing graphene flakes at elevated temperatures would increase their specific capacity at the same charging/discharging current densities as that used for cycling at room temperature.

Keywords Graphene nanoflakes · Li-ion battery · SEI · Temperature · Rate · Capacity

Introduction

The performance of a Li-ion battery largely depends on the structures and properties of its electrodes. The crystal structure of graphite corresponds to a stacking of hexagonal networks of individual layers in the direction perpendicular to the layer plane (*c*-axis) following an A-B stacking arrangement [1]. Lithium intercalation in between the graphene layers leads to the formation of LiC_6 , which results in a low theoretical capacity of graphite that is 372 mA h g^{-1} . Although graphite anodes provide good life cycle performance and high coulombic efficiency [2, 3], they suffer from severe damage in the first cycle due to lithiation and solvent co-intercalation that leads to a drastic drop in the specific capacity [4, 5]. Once a solid electrolyte interphase (SEI) is formed on the electrode surfaces, solvent co-intercalation and, hence, damage is reduced [4, 6] depending on the morphology and uniformity of the SEI [6].

Graphene consists of sp^2 carbon hexagonal networks in which strong covalent bonds are formed between two adjacent carbon atoms [1]. It is argued that for a single graphene layer, lithium could be adsorbed on both sides of the sheet surfaces resulting in formation of Li_2C_6 corresponding to a storage capacity of nearly 744 mA h g^{-1} that is two times that of graphite [7]. Gerouki et al. [8] calculated the specific capacity of graphene sheets of size ~ 0.7 nm as 1488 mA h g^{-1} that corresponded to formation of Li_4C_6 . Therefore, graphene shows potential as a battery anode material because of its large surface area (2600 $\text{m}^2 \text{g}^{-1}$ [9, 10] as well as its high electronic conductivity (sheet resistance $\sim 6 \text{ k}\Omega \text{ sq}^{-1}$) [11–14]. Uthaisar and Barone [15] theoretically investigated Li-ion diffusion in graphene nanoribbons and predicted that lower energy barriers could be found only at a few nanometers from the ribbon-edges leading to faster discharge performance at the edges. Using density functional theory, Pan et al. [9] studied lithium storage in pyrolysis and electron beam irradiation-induced disordered graphene nanosheets (described as having a ripple-like microstructure) and concluded that the observed high capacity of 1013–1054 mA h g^{-1} could be ascribed to the presence of additional reversible storage sites such as edges and other defects. Therefore, increasing the number of edges

✉ Ahmet T. Alpas
aalpas@uwindsor.ca

¹ Engineering Materials Program, Department of Mechanical, Automotive and Materials Engineering, University of Windsor, 401 Sunset Avenue, Windsor, ON N9B 3P4, Canada

in graphene anodes would theoretically improve the charge/discharge performance of lithium-ion batteries.

Experimental studies with single layer graphene, produced by exfoliation of bulk graphite [16], showed a specific capacity of only 540 mA h g⁻¹. Lian et al. [17] prepared graphene sheets with ~ 4 layers through thermal exfoliation and observed that the reversible specific capacity in the first cycle could be as high as 1264 mA h g⁻¹ by charging/discharging at a current density of 0.10 A g⁻¹, and 718 mA h g⁻¹ at a higher current density of 0.50 A g⁻¹. Wu et al. [18] doped graphene with B and N that showed a high reversible capacity of > 1040 mA h g⁻¹ at a low charge/discharge rate of 0.05 A g⁻¹. Moreover, the doped graphene sheets also demonstrated high-rate capability by producing capacities of ~ 199 mA h g⁻¹ (N-doped graphene) and 235 mA h g⁻¹ (B-doped graphene) even at a high rate of 25.00 A g⁻¹. Anodes consisting of MoS₂/SiO₂/graphene hybrids (MSGs) were developed by incorporating amorphous SiO₂ with MoS₂ and graphene nanosheets [19]. MSGs with ~ 40 wt% of SiO₂ and ~ 42 wt% of MoS₂ depicted a stable specific capacity of 1060 mA h g⁻¹ for more than 100 cycles at a current density of 0.1 A g⁻¹. Further, capacity of MSG electrodes lowered to 580 mA h g⁻¹ at a high current density of 8.0 A g⁻¹. Graphene oxide (GO)-based anodes also showed higher capacity at lower rates. For example, Wu et al. [20] prepared anodes consisting of reduced GO enclosed Si/porous carbon nanofibers and obtained a high reversible capacity of 1851.3 mA h g⁻¹ at a low current density of 0.2 A g⁻¹ with negligible capacity fading up to the 50th cycle. When a high current density of 4.0 A g⁻¹ was used, the capacity was recorded as only 421.5 mA h g⁻¹. Guzman et al. [21] dispersed Si nanoparticles on reduced GO sheets and the Si/GO composite anode depicted a high discharge capacity > 2000 mA h g⁻¹ in the first cycle when cycled at a low rate of 0.5 A g⁻¹. The capacity decreased to < 500 mA h g⁻¹ when a high rate of 2.5 A g⁻¹ was used. The measured capacities and the rates reported for

different types of graphene-based anode materials are summarized in Table 1. In general, a high specific capacity of graphene-based anodes was achieved only at low charge/discharge rates.

Li-ion batteries depict limited performance at elevated temperatures, and their cycle life is limited due to surface phenomena on both electrodes that increase their impedance upon cycling [22, 23]. Changes are known to occur both in the electrolyte and the SEI films with the increase in the cycling temperature. Spotnitz et al. [24] performed accelerating rate calorimetry simulations and suggested that the SEI decomposes at temperatures around 70 °C. At still higher temperatures (~ 110 °C), the components of the SEI layers (LiC_x) would react with the electrolyte solvent when carbon-based anodes are used. The electrolyte solvent would decompose only when the cycling temperature exceeds 180 °C [24]. Smart et al. [25] suggested that the SEI films formed on mesocarbon microbead (MCMB) electrodes were protective at high temperatures and prevents further electrolyte reduction at the electrode surfaces. In another work, Smart et al. [26] proposed that Li-ion cells containing electrolytes with higher proportion of EC displayed lower irreversible capacity loss after being exposed to high temperature compared with cells containing low-EC content electrolytes.

This study aims to explore the possibility to achieve high capacity of graphene nanoflake-based anodes at the same charge/discharge rate by cycling at 50 °C. In-situ Raman spectroscopy was performed simultaneously while conducting cyclic voltammetry (CV) experiments to measure solvent intercalation-induced strains in graphene nanoflakes. The observed improvement in the electrochemical performance of graphene nanoflakes due to cycling at an elevated temperature of 50 °C was discussed in terms of the morphology of the SEI and solvent co-intercalation induced strain compared to those observed during cycling graphene at room temperature.

Table 1 Cycling rate dependency of specific capacities as reported in the literature

Graphene-based anode material	Specific capacity at low rate		Specific capacity at high rate		References
	Capacity (mA h g ⁻¹)	Rate (A g ⁻¹)	Capacity (mA h g ⁻¹)	Rate (A g ⁻¹)	
Graphene sheets (~ 4 layers) through thermal exfoliation	1264	0.10	718	0.50	Lian et al. [17]
B- and N-doped graphene	> 1040	0.05	199 (N-doped graphene) 235 (B-doped graphene)	25.00	Wu et al. [18]
40 wt% SiO ₂ /42 wt% MoS ₂ /graphene hybrids	1060	0.10	580	8.00	Han et al. [19]
Reduced GO enclosed Si/porous carbon nanofibers	~ 1851	0.20	~ 422	4.00	Wu et al. [20]
Si/GO composite	> 2000	0.50	< 500	2.50	Guzman et al. [21]

Materials and methods

Description of anode materials and electrochemical experiments

The graphene nanoflakes used in making the anodes had an average thickness of < 3 nm. The lateral dimensions of the flakes were $2\text{--}8\text{ }\mu\text{m}$ (Graphene Laboratories Inc., USA). Raman spectra obtained from the graphene flakes exhibited a G-band at 1580 cm^{-1} as shown in Fig. 1. The formation of this peak was attributed to the in-plane vibration of the sp^2 -hybridized carbon atoms [27, 28]. A small peak was also observed at 1340 cm^{-1} (D-band) that was attributed to structural disorder in the graphene flakes [29, 30]—the edges and cracks within the flakes may contribute to the disorder. The Raman spectrum of graphene was also characterized by a peak at 2700 cm^{-1} (2D or G' [29, 31]) that corresponds to the overtone of the D-band [28]. The height of the 2D-band is an indicator of the number of graphene layers [1]. In Fig. 1, the height of the 2D-band was lower than the G-band indicating a multi-layered structure [32, 33]. The I_{2D}/I_G value was measured from many different locations as well and was found to be 0.62 ± 0.50 —the ratio varied with the number of graphene layers in different stacks that

Fig. 1 Typical Raman spectra obtained from pristine graphene nanoflakes prior to cycling

scattered the laser (2–3 graphene layers in some locations while 50–60 in others).

The anodes were prepared by mixing ultrasonically 80 wt% of graphene flakes with 20 wt% of polyvinylidene fluoride (PVDF)-binder (MTI Corporation, USA) dissolved in 1-methyl-2-pyrrolidinone (99.5%). The slurries prepared in this way were coated on the top surfaces of copper current collectors with surface area of 0.2 cm^2 and the mass loading was calculated as $15.3 \pm 0.3\text{ mg cm}^{-2}$. The electrodes were then dried for 12 h at $105\text{ }^\circ\text{C}$ in an oven and transferred in an Argon glovebox (MBraun LABstar) where H_2O and O_2 levels were maintained below 1 ppm. The electrodes were then mounted in an electrochemical cell inside the glovebox. The electrochemical cell was constructed from polytetrafluoroethylene (PTFE), and had a quartz (optical) glass window on its top surface for monitoring of real time structural changes in the graphene nanoflakes by a Raman objective during the tests. A 99.99% pure Li wire with a resistivity of $9.446\text{ }\mu\Omega\text{-cm}$ (at $20\text{ }^\circ\text{C}$) was used as both the counter electrode and the reference electrode. The electrolyte solution was prepared using 1 M LiClO_4 (99%) in a 1:1 (by vol.) mixture of ethylene carbonate (EC, 99%) and 1,2-dimethoxy ethane (DME, 99%).

Galvanostatic experiments were conducted by initially applying a voltage of 3.00 V and reducing it to 0.02 V (vs. Li/Li^+) using a Potentiostat/Galvanostat system (Solartron Modulab with a data acquisition rate of up to 1.0 MS s^{-1}). The charge/discharge rate used was 0.04 A g^{-1} (current density = 0.60 mA cm^{-2} , which was calculated considering the entire electrode surface area, 19.62 mm^2). CV experiments were conducted between 3.00 V and 0.02 V vs. Li/Li^+ at a constant voltage scan rate of 2.00 mV s^{-1} for measuring the lithiation/delithiation-induced strain in graphene. Both galvanostatic and CV experiments were performed at a temperature of $50\text{ }^\circ\text{C}$. The temperature of the cell was controlled using a heater located at the base of the cell and the temperature was maintained within $\pm 1\text{ }^\circ\text{C}$ of the test temperature.

In-situ Raman spectroscopy and SEM characterization

A $50\times$ objective of a Raman spectrometer (Horiba), equipped with a CCD detector, was used to determine in situ structural changes in graphene nanoflakes during the galvanostatic experiments, as well as to measure the solvent intercalation-induced strain during CV experiments. Raman measurements were performed while the electrodes were installed inside the closed cell. A schematic representation of the experimental setup is shown in Fig. 2. A 50 mW Nd-YAG solid-state laser diode emitting a continuous wave laser at the 532-nm excitation line was used to obtain Raman spectra.

Fig. 2 Schematic representation of the experimental setup used for in situ Raman spectroscopy of surface changes in graphene nanoflake-based anodes cycled in an electrochemical cell with glass window at elevated temperatures

At the end of each experiment, the electrodes consisting of graphene nanoflakes were carefully removed from the electrochemical cell, mounted on stainless steel stubs in ambient air, and transferred to the SEM chamber. An FEI Quanta 200 FEG scanning electron microscope (SEM) and a FEI Magellan 400 SEM with sub-nanometer resolution operated at 1–5 kV was used to study the surface morphologies of the electrodes before and after the electrochemical experiments performed at 25 and 50 °C.

Results and discussion

Charge/discharge profiles during galvanostatic cycling of graphene nanoflakes

An optical image of the graphene electrode obtained at the beginning of the galvanostatic experiments at 3.00 V is shown in Fig. 3a. The laser spot can be seen on the electrode surface. Similar to graphite, graphene was observed to undergo colour change [34] upon a decrease in the voltage, i.e., during the lithium intercalation stage of the galvanostatic experiments, from black in the pristine state to a reddish-yellow intermediate compound at 0.03 V (Fig. 3b) and golden yellow in the fully lithiated electrode at 0.02 V (Fig. 3c). The color is thought to be indicative of the electrode's state-of-charge [34].

The galvanostatic charge/discharge profiles of cycled graphene nanoflakes were recorded for the first and second cycles as shown in Fig. 4a. A prominent plateau was observed at 0.75 V during lithiation of graphene in the first cycle. The presence of this plateau can be attributed to the reduction of the solvent species of the electrolyte and formation of an SEI layer on the surfaces of graphene [35, 36]. The electrolyte has an oxidation potential around 4.70 V vs. Li/Li⁺ and reduction potential close to 0.90 V vs. Li/Li⁺ that defines the electrochemical stability window of the electrolyte [37, 38]. The electrolyte decomposition and subsequent SEI formation on the electrode surface takes place at potentials close to 0.80 V vs. Li/Li⁺ [35, 36]. The electrolyte decomposition potential could vary depending on the current density or voltage scan rate used during the electrochemical experiments [6]. In this case, the reduction of electrolyte occurred at 0.75 V. For experiments conducted at 50 °C, a plateau was observed at a voltage around 0.85 V, which was higher than the voltage at which the plateau formed at 25 °C (0.75 V). Specific capacity was calculated by considering the mass loading of the graphene flakes. At 50 °C, the first cycle specific capacity was as high as 856 mA h g⁻¹ compared to 636 mA h g⁻¹ observed at 25 °C. The enhanced charge and discharge behaviour of graphene at 50 °C may be due to increased and time-dependent lithium insertion within the defects like edges, dislocations, cracks [39], nano-cavities

Fig. 3 In-situ optical images of the graphene nanoflake-based anodes depicting the following colours: **a** black at 3.00 V (no lithium); **b** reddish-yellow at 0.03 V (partially lithiated), and **c** golden yellow at 0.02 V (fully lithiated)

between the graphene flakes and improved adsorption of lithium on each side of the flakes [40, 41].

At the end of the second cycle of the test performed at 25 °C, the capacity was calculated as 294 mA h g⁻¹ that amounted to a capacity loss of 54%. This large irreversible capacity loss can be attributed to the formation of SEI at the surfaces and edges of the graphene flakes [40, 41]. In contrast, the capacity loss was measured as 48% that amounted to a capacity of 445 mA h g⁻¹ at 50 °C in the second cycle. Therefore, by cycling at an elevated temperature, an improvement in the electrochemical performance of graphene flakes was achieved even at the same current

density as opposed to previous observations (see Table 1) that depicted capacity increase only at low rates. The lower capacity observed in the second cycle at 25 °C could be related to the morphology of SEI formed that will be discussed in the following section.

The change in the specific capacity of graphene flakes with the number of cycles were calculated for tests conducted at 25 and 50 °C and the results are plotted in Fig. 4b. During the test performed at 25 °C, the capacity dropped from 636 to 294 mA h g⁻¹ and after the second cycle, the capacity declined gradually. At the end of the 50th cycle, the capacity obtained was as low as 45 mA h g⁻¹. However, for experiments performed at 50 °C, it was observed that the capacity was always higher than that obtained at 25 °C. The capacity measured at 50 °C in the 50th cycle was 134 mA h g⁻¹.

In summary, the specific capacity of graphene nanoflake-based anodes at 50 °C was higher than that at 25 °C. The cyclic performance of graphene would depend on the morphologies of the SEI formed on graphene at these two temperatures, as discussed in the next section.

SEM observations of surfaces of cycled graphene nanoflakes

SEM observations were conducted to investigate the electrochemical cycling induced morphological changes that occurred in the graphene anodes. A secondary electron (SE)-SEM image of an anode consisting of graphene nanoflakes prior to cycling is shown in Fig. 5a. Before cycling, the graphene flakes could be recognized by their dark grey contrast. After 50 galvanostatic cycles, it was observed that the surfaces of the graphene flakes (in completely discharged state) were covered with SEI deposits identified by their brighter contrast, as can be seen in Fig. 5b. The SEI formed at 25 °C was discontinuous and in the form of overlapping deposits or layers, each of size ranging between 50 and 100 nm. In this case, the SEI consisted of large pores and cavities (size ranging from 200 nm to 1 μm) in between and possibly regions of graphene flake surfaces exposed to further electrochemical reduction [6] that could be responsible for the lower capacity at 25 °C as seen in Fig. 4a. The morphology of the graphene surfaces cycled at 50 °C using the same current density showed that the graphene surfaces were completely covered by SEI deposits. Examination of the electrode surfaces showed that the deposits covered the surfaces of the graphene flakes more uniformly. The deposits had a tubular morphology with an intertwined structure (Fig. 5c). Therefore, it can be suggested that a more uniform SEI formed at 50 °C was more stable. It is possible that a stable and uniform SEI assisted in efficient Li-ion diffusion that, in turn, provided the higher capacity

Fig. 4 **a** Charge/discharge profiles obtained during cycling of graphene nanoflake-based anodes at 25 and 50 °C and **b** specific capacities of graphene flakes at 25 and 50 °C using a charge/discharge rate of 0.04 Ag^{-1}

to graphene [42]. Previously it was observed that the SEI films formed on graphite-based anodes, after cycling in EC-based electrolytes, consisted of crystalline domains

enclosed in an amorphous matrix [6]. The crystalline domains in the SEI primarily consisted of Li_2CO_3 that were thought to enhance Li-ion diffusivity across the

Fig. 5 SE-SEM images obtained from graphene nanoflake-based anodes **a** before cycling and after 50 cycles at **b** 25 °C and **c** 50 °C

electrode/electrolyte interface [6, 43]. It is to be noted that a fraction of the SEI could be lost when exposed to the high voltage electron beam inside the vacuum chamber of the SEM. However, care was taken such that the areas on the electrode surfaces that were exposed to

the beam for longer durations were not considered for analyses.

Measurement of intercalation-induced strain and disorder in graphene nanoflakes using Raman spectroscopy

Raman spectroscopy was performed to record changes in the surface characteristics of the graphene flakes as a function of the Li-ion cell temperature (25 and 50 °C) and the results are shown in Fig. 6. The Raman spectrum of anodes containing graphene flakes before cycling indicated that the intensity of the D-band at 1340 cm^{-1} increased slightly compared to that observed in as-received condition in Fig. 1. The increased intensity was attributed to an increase in the structural disorder in the graphene flakes by means of ultrasonication during the electrode preparation. The intensity ratio of the G-band (I_G) to the D-band (I_D), I_D/I_G was 0.40 before cycling. At the end of 50 galvanostatic cycles at 25 °C, the ratio of I_D/I_G increased to 1.06 as the intensity of the D-band increased. The increase in the intensity of the D-band was due to increase in disorder by the formation of new defects possibly as a result of creation of new edges during fracture of the graphene flakes caused by cycling. In addition, binding of lithium to the newly formed edges and defects would also increase the intensity of the D-band. Figure 6 also shows the Raman spectrum obtained from the graphene surfaces subjected to 50 galvanostatic cycles at 50 °C. The D-band had a high intensity and the I_D/I_G ($= 1.02$) calculated in this case was comparable to that obtained during cycling at 25 °C. In addition, the ratio of I_G to the intensity of the 2D-band (I_{2D}), I_{2D}/I_G , increased from 0.60 before cycling, to 0.80 after cycling at 25 °C, and to 0.79 at 50 °C. The increase in the I_{2D}/I_G ratios could be also attributed to generation of cycling-induced defects in the graphene flakes. Although the amount of disorder induced during cycling was almost the same in both cases, it should be noted that the capacity obtained at 50 °C (856 mA h g^{-1}) was 35% higher than that obtained at 25 °C (Fig. 4a) possibly due to formation of a stable SEI at that temperature as shown in Fig. 5c.

The process of lithiation would induce strains in the electrode materials' lattices. In order to determine the variations in the strain generated during voltage cycling, in situ Raman spectroscopy was performed simultaneously with the CV experiments conducted between $3.00\text{ V} \rightarrow 0.02\text{ V} \rightarrow 3.00\text{ V}$ vs. Li/Li^+ at a scan rate of 2.00 mV s^{-1} . The cyclic voltammograms obtained during cycling at 25 and 50 °C are shown in Fig. 7. The CV curve obtained during cycling of graphene flakes at 25 °C showed a cathodic reduction voltage peak at 0.75 V and for the curve obtained at 50 °C, the peak appeared at 0.85 V. The occurrence of the voltage peaks at 0.75 V (25 °C) and 0.85 V (50 °C) were in agreement with the voltage of the plateaus obtained during galvanostatic cycling of the graphene

Fig. 6 Raman spectra obtained from graphene nanoflake-based anodes before cycling and after 50 cycles at 25 and 50 °C

electrodes (Fig. 4a). Formation of these peaks could be attributed to the formation of an SEI layer on the surfaces of the graphene flakes as a result of reduction of the electrolyte [44].

A series of in situ Raman spectra obtained during these CV experiments at 3.00, 0.20 and 0.02 V showed that the G-band of graphene shifted from 1580 cm⁻¹ (at 3.00 V) to higher frequency shifts with the decrease in the voltage from 3.00 V (Fig. 8). For example, the G-band shifted from 1580 cm⁻¹ at 3.00 V to 1597 cm⁻¹ at 0.02 V for the graphene flakes cycled at 25 °C, as seen in Fig. 8a. The G-band shifted to only 1583 cm⁻¹ when the voltage was decreased to 0.02 V during cycling of graphene flakes at 50 °C (Fig. 8b). The frequency shift of the G-band can be related to the uniaxial strain and the shear strain—but the latter could be ignored due to its minor contribution [45]. The relation between the Raman frequency and the strain could be expressed as [45, 46]:

$$\frac{\Delta\omega}{\omega_o} = \gamma(\varepsilon_{xx} + \varepsilon_{yy}) \quad (1)$$

where ω_o is the G-band frequency; $\Delta\omega$ is the shift in the frequency; $\gamma = 1.80$ is the Grüneisen parameter for graphene

[47, 48]; ε_{xx} is the uniaxial strain, and $\varepsilon_{yy} \approx -0.2 \varepsilon_{xx}$ is the relative strain in the perpendicular direction according to the Poisson's ratio of graphene ($= 0.19$ [49]). From these values, the maximum ε_{xx} for graphene nanoflakes cycled at 25 °C was calculated as 7.5×10^{-3} . During the reverse sweep, the G-band shifted back to 1580 cm⁻¹ when the voltage was increased to 3.00 V. The shift in the location of the G-band was previously discussed in terms of the strain increase in the multilayered graphene [50, 51]. It could be attributed to intercalation of solvent molecules [43]. The changes in the uniaxial strain are plotted as a function of the time and voltage in Fig. 8c. A smaller shift in the location of the G-band was observed in case of graphene cycled at 50 °C, compared to that observed in case of graphene cycled at 25 °C ($0.75 \pm 0.02\%$). This could be attributed to a decrease in the strain to $0.12 \pm 0.03\%$. Using in situ Raman spectroscopy, the cycling-induced strain in the graphite lattice was estimated as $0.41 \pm 0.01\%$, which was accompanied by surface degradation of graphite electrodes [43]. Thus, it can be suggested that graphene could accommodate a high strain due

Fig. 7 Cyclic voltammograms obtained from graphene nanoflake-based anodes cycled at 25 and 50 °C using a voltage scan rate of 2.00 mV s⁻¹

to lithiation and solvent co-intercalation at 25 °C, yet, the strain in graphene nanoflakes could be reduced if the Li-ion cell is cycled at an elevated temperature of 50 °C. This will also yield a 35% higher specific capacity in the first cycle as described earlier. Although the mechanisms of lithium storage in graphene should be further clarified, a possible reason for the enhanced capacity of graphene at elevated temperatures could be due to the formation of additional sites in the graphene nanoflakes for accommodation of Li-ions [16] and the electrochemical capacity of graphene would depend on the defect density as the defects act as Li-ion storage sites [39–41]. The improved capacity would also depend on the composition of the SEI films formed on the anode surfaces [25, 26, 52]. For example, thermal pre-treatment of Li-ion cells containing graphite anodes at 60 °C [42] caused the formation of a Li₂CO₃-enriched SEI that enhanced the capacity by 28% compared to that at 25 °C. An SEI enriched with Li₂CO₃ is known to provide facile diffusion paths for Li-ions across the SEI [53].

In summary, the results suggested that the capacity of graphene flakes would further increase if graphene is pre-cycled

at elevated temperatures that would cause formation of a more uniform and stable SEI possibly due to the faster Li-ion diffusion kinetics. An SEI generated in this way is expected to reduce solvent co-intercalation and provide a higher specific capacity even at the same charging current.

Summary and conclusions

Li-ion cell anodes fabricated from graphene nanoflakes were subjected to galvanostatic cycling at temperatures of 25 and 50 °C. In-situ Raman spectroscopy was used to investigate the cycling-induced strain generation in the graphene nanoflakes. High-resolution SEM images were used to study the morphologies of the SEI formed on graphene. The main conclusions arising from these investigations are as follows:

1. The specific capacity of graphene nanoflake-based anodes increased by 35% in the first cycle—from 636 mA h g⁻¹ at 25 °C, to 856 mA h g⁻¹ at 50 °C, at the same rate of 0.04 A g⁻¹.

Fig. 8 In-situ Raman spectra obtained from graphene nanoflake-based anodes cycled at **a** 25 °C and **b** 50 °C, while scanning from 3.00 → 0.02 → 3.00 V at a scan rate of 2.00 mV s⁻¹. **c** Plot showing changes in the uniaxial strain measured from the shift in the Raman G-band observed in **a**, **b**

- The amount of disorder ($I_D/I_G = 1.02$ – 1.06) induced during cycling was almost the same at both temperatures. The capacity enhancement that occurred at 50 °C was

likely to be prompted by the formation of a stable and uniform SEI at that temperature.

3. The SEI formed at 50 °C reduced solvent co-intercalation induced strain in graphene from 0.75% (at 25 °C) to 0.12%.

In summary, prior to commercial use of Li-ion cells containing graphene-based anodes, a thermal pre-cycling step at an elevated temperature will yield a 35% higher specific capacity even when operated at the same rate that was used for charging at room temperature.

Acknowledgements The financial support provided by the Natural Sciences and Engineering Research Council (NSERC) of Canada in the form of a Discovery Grant is gratefully acknowledged.

Open Access This article is distributed under the terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

References

1. Malard, L.M., Pimenta, M.A., Dresselhaus, G., Dresselhaus, M.S.: Raman spectroscopy in graphene. *Phys. Reports* **473**, 51–87 (2009)
2. Liang, M.H., Zhi, L.J.: Graphene-based electrode materials for rechargeable lithium batteries. *J. Mater. Chem.* **19**, 5871–5878 (2009)
3. Liu, C., Li, F., Ma, L.P., Cheng, H.M.: Advanced materials for energy storage. *Adv. Mater.* **22**, E28–E62 (2010)
4. Bhattacharya, S., Riahi, A.R., Alpas, A.T.: In-situ observations of lithiation/de-lithiation induced graphite damage during electrochemical cycling. *Scripta Mater.* **64**, 165–168 (2011)
5. Bhattacharya, S., Riahi, A.R., Alpas, A.T.: A transmission electron microscope study of crack formation and propagation in electrochemically cycled graphite electrode in lithium-ion cells. *J. Power Sources* **196**, 8719–8727 (2011)
6. Bhattacharya, S., Alpas, A.T.: Micromechanisms of solid electrolyte interphase formation on electrochemically cycled graphite electrodes in lithium-ion cells. *Carbon* **50**, 5359–5371 (2012)
7. Dahn, J.R., Zheng, T., Liu, Y., Xue, J.S.: Mechanisms for lithium insertion in carbonaceous materials. *Science* **270**, 590–593 (1995)
8. Gerouki, A., Goldner, M.A., Goldner, R.B., Haas, T.E., Liu, T.Y., Slaven, S.: Density of states calculations of small diameter single graphene sheets. *J. Electrochem. Soc.* **143**, L262–L263 (1996)
9. Pan, D.Y., Wang, S., Zhao, B., Wu, M.H., Zhang, H.J., Wang, Y., Jiao, Z.: Li storage properties of disordered graphene nanosheets. *Chem. Mater.* **21**, 3136–3142 (2009)
10. Su, D.S., Schlögl, R.: Nanostructured carbon and carbon nanocomposites for electrochemical energy storage applications. *Chem. Sus. Chem.* **3**, 136–168 (2010)
11. Sun, Y.Q., Wu, Q.O., Shi, G.Q.: Graphene based new energy materials. *Energy Environ. Sci.* **4**, 1113–1132 (2011)
12. Banks, C.E., Brownson, D.B., Brownson, D.A.C., Kampouris, D.K.: An overview of graphene in energy production and storage applications. *J. Power Sources* **196**, 4873–4885 (2011)
13. Pumera, M.: Graphene-based nanomaterials for energy storage. *Energy Environ. Sci.* **4**, 668–674 (2011)
14. Guo, C.X., Wang, M., Chen, T., Lou, X.W., Li, C.M.: A hierarchically nanostructured composite of MnO₂/conjugated polymer/graphene for high-performance Lithium ion batteries. *Adv. Energy Mater.* **1**, 736–741 (2011)
15. Uthaisar, C., Barone, V.: Edge effects on the characteristics of Li diffusion in graphene. *Nano Lett.* **10**, 2838–2842 (2010)
16. Yoo, E., Kim, J., Hosono, E., Zhou, H.S., Kudo, T., Honma, I.: Large reversible Li storage of graphene nanosheet families for use in rechargeable lithium ion batteries. *Nano Lett.* **8**, 2277–2282 (2008)
17. Lian, P., Zhu, X., Liang, S., Li, Z., Yang, W., Wang, H.: Large reversible capacity of high quality graphene sheets as an anode material for lithium-ion batteries. *Electrochim. Acta* **55**, 3909–3914 (2010)
18. Wu, Z.S., Ren, W., Xu, L., Li, F., Cheng, H.M.: Doped graphene sheets as anode materials with superhigh rate and large capacity for lithium ion batteries. *ACS Nano* **5**, 5463–5471 (2011)
19. Han, S., Zhao, Y., Tang, Y., Tan, F., Huang, Y., Feng, X., Wu, D.: Ternary MoS₂/SiO₂/graphene hybrids for high-performance lithium storage. *Carbon* **81**, 203–209 (2015)
20. Wu, C., Lin, J., Chu, R., Zheng, J., Chen, Y., Zhang, J., Guo, H.: Reduced graphene oxide as a dual-functional enhancer wrapped over silicon/porous carbon nanofibers for high-performance lithium-ion battery anodes. *J. Mater. Sci.* **52**, 7984–7996 (2017)
21. Guzman, R.C., Yang, J., Cheng, M.M.C., Salley, S.O., Ng, K.Y.S.: A silicon nanoparticle/reduced graphene oxide composite anode with excellent nanoparticle dispersion to improve lithium ion battery performance. *J. Mater. Sci.* **48**, 4823–4833 (2013)
22. Aurbach, D., Markovsky, B., Rodkin, A., Levi, E., Cohen, Y.S., Kim, H.-J., Schmidt, M.: On the capacity fading of LiCoO₂ intercalation electrodes: the effect of cycling, storage, temperature, and surface film forming additives. *Electrochim. Acta* **47**, 4291–4306 (2002)
23. Aurbach, D., Talyosef, Y., Markovsky, B., Markevich, E., Zinigrad, E., Asraf, L., Gnanaraj, J.S., Kim, H.J.: Design of electrolyte solutions for Li and Li-ion batteries: a review. *Electrochim. Acta* **50**, 247–254 (2004)
24. Spotnitz, R., Franklin, J.: Abuse behavior of high-power, lithium-ion cells. *J. Power Sources* **113**, 81–100 (2003)
25. Smart, M.C., Ratnakumar, B.V., Whitacre, J., Whitcanack, L., Chin, K., Rodriguez, M., Surampudi, S.: The effect of high temperature exposure upon the performance of lithium ion cells. Seventeenth Annual Battery Conference on Applications and Advances. Proceedings of Conference (Cat. No.02TH8576). Long Beach, CA, pp. 53–58 (2002)
26. Smart, M.C., Ratnakumar, B.V., Whitacre, J.F., Whitcanack, L.D., Chin, K.B., Rodriguez, M.D., Zhao, D., Greenbaum, S.G., Surampudi, S.: Effect of electrolyte type upon the high-temperature resilience of lithium-ion cells. *J. Electrochem. Soc.* **152**, A1096–A1104 (2005)
27. Tuinstra, F., Koenig, J.L.: Raman spectrum of graphite. *J. Chem. Phys.* **53**, 1126–1130 (1970)
28. Pimenta, M.A., Dresselhaus, G., Dresselhaus, M.S., Cançado, L.G., Jorio, A., Saito, R.: Studying disorder in graphite-based systems by Raman spectroscopy. *Phys. Chem. Chem. Phys.* **9**, 1276–1290 (2007)
29. Ferrari, A.C.: Raman spectroscopy of graphene and graphite: disorder, electron-phonon coupling, doping and nonadiabatic effects. *Solid State Commun.* **143**, 47–57 (2007)
30. Jaber-Ansari, L., Puntambekar, K.P., Tavassol, H., Yildirim, H., Kinaci, A., Kumar, R., Saldaña, S.J., Gewirth, A.A., Greeley, J.P., Chan, M.K.Y., Hersam, M.C.: Defect evolution in graphene upon electrochemical lithiation. *ACS Appl. Mater. Interfaces* **6**, 17626–17636 (2014)

31. Vidano, R.P., Fishbach, D.B., Willis, L.J., Loehr, T.M.: Observation of Raman band shifting with excitation wavelength for carbons and graphites. *Solid State Commun.* **39**, 341–344 (1981)
32. Yoon, S.M., Choi, W.M., Baik, H., Shin, H.J., Song, I., Kwon, M.S., Bae, J.J., Kim, H., Lee, Y.H., Choi, J.Y.: Synthesis of multilayer graphene balls by carbon segregation from nickel nanoparticles. *ACS Nano* **6**, 6803–6811 (2012)
33. Radhakrishnan, G., Cardema, J.D., Adams, P.M., Kim, H.I., Foran, B.: Fabrication and electrochemical characterization of single and multi-layer graphene anodes for lithium-ion batteries. *J. Electrochem. Soc.* **159**, A752–A761 (2012)
34. Maire, P., Evans, A., Kaiser, H., Scheifele, W., Novák, P.: Colorimetric determination of lithium content in electrodes of lithium-ion batteries. *J. Electrochem. Soc.* **155**, A862–A865 (2008)
35. Peled, E.: The electrochemical behavior of alkali and alkaline earth metals in nonaqueous battery systems—the solid electrolyte interphase mode. *J. Electrochem. Soc.* **126**, 2047–2051 (1979)
36. Vargas, Ó., Caballero, Á., Morales, J., Castellón, E.R.: Contribution to the understanding of capacity fading in graphene nanosheets acting as an anode in full Li-ion batteries. *ACS Appl. Mater. Interfaces* **6**, 3290–3298 (2014)
37. An, S.J., Li, J., Daniel, C., Mohanty, D., Nagpure, S., Wood III, D.L.: The state of understanding of the lithium-ion-battery graphite solid electrolyte interphase (SEI) and its relationship to formation cycling. *Carbon* **105**, 52–76 (2016)
38. Winter, M., Appel, W.K., Evers, B., Hodal, T., Möller, K.C., Schneider, I., Wachtler, M., Wagner, M.R., Wrodnigg, G.H., Besenhard, J.O.: Studies on the anode/electrolyte interface in lithium ion batteries. *Monatsh. Chem.* **132**, 473–486 (2001)
39. Das, A., Chakraborty, B., Sood, A.K.: Raman spectroscopy of graphene on different substrates and influence of defects. *Bull. Mater. Sci.* **31**, 579–584 (2008)
40. Wang, G., Shen, X., Yao, J., Park, J.: Graphene nanosheets for enhanced lithium storage in lithium ion batteries. *Carbon* **47**, 2049–2053 (2009)
41. Kokai, F., Sorin, R., Chigusa, H., Hanai, K., Koshio, A., Ishihara, M., Koga, Y., Hasegawa, M., Imanishi, N., Takeda, Y.: Ultrasonication fabrication of high quality multilayer graphene flakes and their characterization as anodes for lithium ion batteries. *Diam. Relat. Mater.* **29**, 63–68 (2012)
42. Bhattacharya, S., Riahi, A.R., Alpas, A.T.: Thermal cycling induced capacity enhancement of graphite anodes in lithium-ion cells. *Carbon* **67**, 592–606 (2014)
43. Bhattacharya, S., Riahi, A.R., Alpas, A.T.: Electrochemical cycling behaviour of lithium carbonate (Li_2CO_3) pre-treated graphite anodes—SEI formation and graphite damage mechanisms. *Carbon* **77**, 99–112 (2014)
44. Novák, P., Joho, F., Lanz, M., Rykart, B., Panitz, J.C., Alliata, D., Kötz, R., Haas, O.: The complex electrochemistry of graphite electrodes in lithium-ion batteries. *J. Power Sources* **97–98**, 39–46 (2001)
45. Reich, S., Jantoljak, H., Thomsen, C.: Shear strain in carbon nanotubes under hydrostatic pressure. *Phys. Rev. B* **61**, R13389–R13392 (2000)
46. Thomsen, C., Reich, S., Ordejon, P.: Ab initio determination of the phonon deformation potentials of graphene. *Phys. Rev. B* **65**, 073403/1–073403/3 (2002)
47. Ding, F., Ji, H., Chen, Y., Herklotz, A., Dörr, K., Mei, Y., Rastelli, A., Schmidt, O.G.: Stretchable graphene: a close look at fundamental parameters through biaxial straining. *Nano Lett.* **10**, 3453–3458 (2010)
48. Cheng, Y.C., Zhu, Z.Y., Huang, G.S., Schwingenschlögl, U.: Grüneisen parameter of the G mode of strained monolayer graphene. *Phys. Rev. B* **83**, 115449 (2011)
49. Politano, A., Chiarello, G.: Probing the Young's modulus and Poisson's ratio in graphene/metal interfaces and graphite: a comparative study. *Nano Res.* **8**, 1847–1856 (2015)
50. Panitz, J.C., Joho, F., Novak, P.: In situ characterization of a graphite electrode in a secondary lithium-ion battery using Raman microscopy. *Appl. Spectrosc.* **53**, 1188–1199 (1999)
51. Qi, Y., Harris, S.J.: In situ observation of strains during lithiation of a graphite electrode. *J. Electrochem. Soc.* **157**, A741–A747 (2010)
52. Leng, F., Tan, C.M., Pecht, M.: Effect of temperature on the aging rate of Li ion battery operating above room temperature. *Scientific Reports* **5**(12967), 1–12 (2015)
53. Shi, S., Qi, Y., Li, H., Hector Jr., L.G.: Defect thermodynamics and diffusion mechanisms in Li_2CO_3 and implications for the solid electrolyte interphase in Li-ion batteries. *J. Phys. Chem. C* **117**, 8579–8593 (2013)