On the Reliability of Sodium Co-Intercalation in Expanded Graphite Prepared by Different Methods as Anodes for Sodium-Ion Batteries

Marta Cabello, a Xue Bai, a Taras Chyrka, b Gregorio F. Ortiz, a, d Pedro Lavela, a Ricardo Alcántara, a, d and José L. Tirado a, d, e

a Departamento de Química Inorgánica e Ingeniería Química, Instituto Universitario de Investigación en Química Fina y Nanoquímica, Universidad de Córdoba, Campus de Rabanales, Edificio Marie Curie, E-14071 Córdoba, Spain
b Scientific research centre “Resource saving technologies”, National Technical University of Ukraine “Kyiv polytechnic institute”, 03056 Kyiv, Ukraine

Recent improvements of sodium ion batteries have been achieved by the use of graphitic carbon as an anode and glyme-based electrolytes. In this work, expanded graphites are prepared by thermal expansion, Brodie and Hummer’s modified methods. Their structural, morphological and electrochemical properties are compared with those of the original natural graphite. XRD patterns, XPS and Raman spectra corroborate the presence of graphite oxide intermediates and reveal different reduced forms of expanded graphite which can affect the sodium insertion properties. The use of sodium triflate in diglyme enhanced the electrochemical performance in terms of delivering a flat plateau at ca. 0.65 and 0.55 V in discharge/charge cycles. The thermally expanded graphite increased the capacity and efficiency from 100 to 115 mA h g⁻¹ and from 93 to 96% over 100 cycles when cycled at C rate as compared to natural graphite. Ex-situ XRD patterns reveal the presence of new set of reflections ascribable to sodium ordering in different stages as evidenced by the calculated Patterson diagrams. The new results described here would account for development of carbon-based material and their prospects and challenges for sodium ion battery anodes.

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The sodium intercalation into graphite is still one of the most interesting and unusual in the solid state chemistry of intercalation compounds. Neither ionic nor hard sphere model theory explains why the liquid phase interaction of molten sodium with graphite provides only high-stage compositions.¹² This effect contrasts with that for other alkali metals,³ in which first-stage graphite intercalation compounds (GICs) can be easily obtained. Uddød suggested that the discrepancy between the size of sodium atoms and the distances between potential minima in the graphite sheet causes the absence of low-stage Na-GICs.⁴

Graphite has a long-range-ordered layered structure where Li⁺ ion can be easily intercalated between the graphene layers by electrochemical means. The main lithium insertion reaction occurs at a flat plateau around 0.2 V, and the capacity is 372 mAh g⁻¹.⁵,⁶ Unlike, the graphite anode does not intercalate sodium to any appreciable extend. The galvanostatic curves during the full sodiation/desodiation shows a monotonic voltage curves, which capacity is lower than 35 mAh g⁻¹.⁷,⁸ This normally refers to the standard electrolytes that are based on organic carbonates (EC ethylene carbonate, DMC dimethylcarbonate) and lithium salts (LiPF₆) or sodium salts (NaPF₆).

In the search for alternative secondary batteries that will replace lithium ion batteries (LIBs), sodium ion batteries (SIBs) have received attention due to the following reasons: (i) abundance of sodium sources (it is the 4th most abundant element in the earth crust), (ii) the low cost of sodium compared to lithium, especially for large-scale electric storage applications, and (iii) the similar chemistry of sodium and lithium.⁹ So far, several issues have scoffed at the optimal performance of graphite anodes at both lithium ion (LIB) and sodium ion batteries (SIB). For instance: (i) the risk of inserting alkali metals near to 0 V is known to jeopardize the safety in batteries, and (ii) the lack of a flat plateau during sodium insertion hinders the manufacturing of carbon-based commercial sodium-ion batteries. The engineering knowledge developed until lately for successful SIBs can be influenced to ensure rapid progress in this area, although distinct electrolytes and functional carbon materials will be required for dual intercalation systems based on sodium.

Regarding the electrolyte, systems based on poly(ethylene oxide), PEO, with dissolved alkali metal salts have received significant attention as polymer electrolytes.¹⁰ Glymes are glycol dimethoxy ethers with the general formula CH₃O(CH₂)ₙ(CH₃)OCH₃, which are PEO analogue with low molecular weight (n<6).¹¹ Glymes based electrolytes have been recently proposed as new electrolyte for SIB.¹²,¹³ Indeed, Kim et al. reported unusual Na storage behavior in natural graphite through Na⁺-solvent co-intercalation combined with pseudocapacitive behaviors using ether-based electrolytes.¹⁴,¹⁵ Jache et al. demonstrated that graphite may insert sodium by using cointercalation phenomena in a diglyme-based electrolyte.¹⁶ Zhu et al. showed the sodium storage performance of graphite in linear ether-based electrolytes using sodium perchlorate and/or sodium triflate in tetraglyme (TGM), diglyme (DGM), and 1,2-dimethoxyethane (DME).¹⁷ However, the mechanism of ionic transport is not already well understood. Some results revealed that in polymer electrolytes with bendable backbones, the ionic transport is highly coupled to the relaxation processes of the polymer backbone.¹⁸,¹⁹ Also, it is suggested that the anion plays a role in the transport of cations, either through correlated motion of cations and anions or via transport of cation-anion clusters.²⁰,²¹

Regarding the carbon material, the influence of several factors such as heteroelement contents,²² structural differences in soft and hard carbons,²³,²⁴ morphological properties (nanowires, nanotubes, microbeads reduced graphene oxides or hollow carbon nanoparticles),²⁵,²⁶ have been investigated as anodes for SIBs using standard electrolytes. Nonetheless, it is needed a further progress in the preparation of C-based materials.

The Na-ion battery system is potentially promising power sources for encouraging the substantial use of low-cost energy storage systems. The design of a full cell with stable energy density requires using suitable materials exhibiting flat plateau. While for the cathode there are many compounds showing flat plateau, in the anode this characteristic has been barely reported.

In this work we report the use of expanded graphites as a Na-ion battery anode. They are obtained from natural graphite (GSM) using three different approaches: i) by means of fast heating of graphite bisulfate precursors, ii) Brodie and iii) Hummer’s modified methods. The interlayer spacing of expanded graphite can be tailored by controlled oxidation and reduction processing. An entire physico-chemical and electrochemical characterization of the electrodes is presented. The insertion properties of sodium into different kind of graphite are described by electrochemical means. We have found that using diglyme-based electrolyte (different to standard electrolytes)
is possible to achieve flat plateau in a safe voltage windows during cycling.

Experimental

Raw material is natural flake crystalline graphite (GSM). Ther- mally expanded graphite (TEG) is obtained by fast heating of graphite bisulfate at 1400°C during less 1 s. The thermal treatment can be described as following (Fig. S1). Using compressed air, the dried oxidized graphite is supplied with speed of 1 m s⁻¹ through the nipple 1 to the mixing chamber 2, where simultaneously primary air is supplied for combustion. Additionally to the chamber 2, secondary air is going through the nipple 3 composing necessary stoichiometric ratio 1:10 (natural gas-air). Gas is supplied through the nipple 4 to the chamber 2. Obtained mixture is passing to the turbulent chamber 5, where spontaneous combustion occurs that causes temperature rise up to 1400°C. During short time intercalated compounds (sulfuric acid) decompose converting to the gas products and cause expansion of graphite. Thermally expanded graphite surrounded by combustion products goes out to the burning chamber, where particulate calcination occurs. Then graphite is directed to the calcinating furnace.

Another different procedure to get expanded graphite is based on a two-step oxidation-reduction process. For that purpose, the Brodie35 and Hummer's34 modified methods were used to compare the effects on the carbon structure with the previous method. For Brodie’s method, natural graphite GSM (1 g), nitric acid 65% (30 ml) and sodium chlorate (7.5 g) were used. This mixture was magnetically stirred (24, 92, and 144 h) at room temperature and washed in distilled water until reaching a neutral pH. Then, the graphite oxide (GO) was dried at 60°C overnight. Eventually, GO is thermally reduced (500, 1000 and 1300°C) under Ar atmosphere for 3 h.

For Hummer’s method, natural graphite GSM (1g) and 0.5 g of NaNO₃ were added into 23 mL of sulfuric acid (98%) in a round-bottomed flask that was previously cooled into an ice bath for 20 min ensuring temperature about 5–7°C. Then, three grams of KMN₃O₆ were slowly added into the mixture while stirring, keeping the temperature at about 5–7°C. This mixture is stirred during 30 min under the ice bath to release gas under continuous stirring. Then, distilled water (46 mL) was added slowly, which produced a rapid increase in the solution temperature. The reaction was held for 30 min to increase the oxidation degree of the GO. Afterwards, 140 mL of distilled water and 20 mL of hydrogen peroxide (H₂O₂, 30%) are added to the solution. In order to wash the solid, the resultant product was transferred to a beaker containing 150 mL of water and then it was settle down overnight and water was poured. The last step was repeated until the supernatant water was pH neutral. After that, the GO is dried in air atmosphere at 60°C overnight. Eventually, oxidized graphites were thermally reduced (500, 1000 and 1300°C) in Ar atmosphere for 3 h.

The electrochemical measurements were performed with Swagelok type cells assembled in an argon-filled glove box (MBraun Lab master 130). For this purpose, carbon-based electrodes were composed by active material (92%) and PVDF (polyvinylidene fluoride) (8%). The electrode is vacuum dried at 120°C for at least two hours. The sodium half cell consists of metallic sodium as anode (disc of 9 mm), the electrolyte, and the C-based electrode as cathode. The electrodes were separated by glass fiber disks (GF/A-Whatman) impregnated in the electrolyte solution. The cells were assembled in an argon filled glove box under controlled O₂ (2 ppm) and H₂O (1 ppm) traces. The sodium half cells were cycled by the galvanostatic method between 0.003 and 3.0 V at different rates (C/10, C/2, C and 2C). All the electrochemical experiments were monitored in a galvanostat/potentiostat VMP system. Several electrolyte solutions were tested: (i) 1 M NaOTf (NaCF₃SO₃ or sodium triflate, 98%, Aldrich), dissolved in DGM (diglyme 99%, Sigma-Aldrich), (ii) 1 M NaPF₆ (99%, Strem Chemicals) dissolved in DGM, (iii) 1 M NaPF₆ dissolved in EC:DEC (99%, Aldrich) and (iv) 1 M NaClO₄ in EC:DEC. The melting and boiling points of the diglyme are −64°C (209 K) and 162°C (435 K), respectively. The electrolyte based on NaClO₄ in PC (propylene carbonate) is not studied in these experiments because the PC solvent can be co-intercalated into graphite causing exfoliation.35

Results and Discussion

Natural graphite (GSM) revealed an intense crystalline (002) peak at 26.55° corresponding to an interlayer distance of d₀₀₂ = 3.357 Å,6,36 and a small shoulder at 26.2° (Fig. 1 and Fig. S2). Due to the oxidation and subsequent partial reduction of graphite, a shifting and broadening of the (002) peak is observed. The thermally expanded graphite (TEG) exhibits an asymmetric reflection at 26.28° and a shoulder at 26.53°. It involves a slight increase of the interlayer distance (d₀₀₂ = 3.388 Å) as compared to GSM, while the crystallite size (Lc) decreased from 37.65 nm to 17.86 nm for TEG (Table S1). The calculated unit cell parameters are included in Table S1. When using Hummer’s modified method, the oxidized graphite is successfully formed (sample labeled as GSM-H(1h)) as evidenced by the development of the new (001) peak appearing at 10.5° (d₀₀₁ = 8.418 Å, in Fig. S2). The large interlayer spacing of the GSM-H(1h) sample can be attributed to the oxygenated functional groups introduced by the harsh oxidation treatment of graphite.36–38 The full oxidation in GSM-H(1h) sample is not achieved as evidenced by the presence of a (002) peak of graphite with an asymmetric shape located at 25.84° (d₀₀₂ = 3.445 Å, Fig. 1) and crystallite size of 6 nm. In turn, when using the Brodie’s method (sample labeled as GSM-B(24h)), the peak ascribable to graphite oxide (≈10.5°) is not observed. This method leads to a less extensive oxidation degree (Fig. S2). However, after the reduction process a shifting and broadening of the (002) peak with a maximum at 25.93° (d₀₀₂ = 3.352Å) and a crystallite size of 8.46 nm is observed (Fig. 1). As expected, the patterns recorded for reduced samples (labeled as GSM-HR and GSM-BR in Fig. 1 and Fig. S2) revealed that the diffraction peaks shift back to 20 ≈ 26.3°. These values are still smaller than that of original natural graphite (GSM) that appeared at 26.55°. The crystallite size (Lc) measured after the thermal reduction at 1000°C is 9.66 and 15.84 nm for GSM-HR and GSM-BR samples, respectively (Table S1, Fig. 1). The partial reduction at 1300°C has an enlarged interlayer spacing of 3.7 Å. In summary, these chemically treated GSM samples preserved the graphite-like structure with a larger inter-planar distance.

Gathering more detailed information about the level of graphitization of carbon materials will be crucial for understanding the influence of sodium insertion properties. For that, Raman spectra were recorded in the region between 750 and 2000 cm⁻¹ (Fig. 2). The spectrum of GSM is mainly characterized by the contribution from the G band which represents the in-plane displacement of the ordered carbons couples in the hexagonal sheets.39 The fitting for the GSM sample is composed by two peaks. The main peak at ca. 1580 cm⁻¹ corresponds to an ideal graphic lattice vibration mode with E₂g symmetry and
was fitted with Lorentz Amp Function. The small D1 bands at ca. 1350 cm$^{-1}$ corresponds to the lack of long-range translation symmetry in the disordered carbon and was fitted with Gauss Amp Function. Although TEG sample showed a similar profile, the graphitization index ($I_{D}/I_{G}$) is higher for TEG as compared to GSM (Table I), which could be indicative of a full reduction of graphene layers observed by Raman. In addition, the in-plane correlation length ($L_a$) has been calculated from the following equation:

$$I_{D}/I_{G} = C/L_a$$  \[1\]

where $C$ depends on the Raman laser excitation energy ($C = 50$ for $\lambda = 532$ nm). The spectra of GSM-B and GSM-H exhibit a relative enhancement of the D1 and consequently a decrease of the graphitization index (Table II). Moreover, new contributions ascribable to disordered local environments, named as D2, D3 and D4, are observed. Note that D2 is observed as a shoulder on the part of G band and it shares the same $E_{2g}$ symmetry vibration mode with G band. D2 corresponds to a disordered graphitic lattice mode and the disorder comes from the surface graphene layers. The D3 band appears between D1 and G bands and represents the amorphous carbon at interstitial defects (such as organic molecules fragments or functional groups). Besides that, the peak from D1 exhibits another shoulder at around 1200 cm$^{-1}$, which is found as D4 with disordered graphitic lattice ($A_{1g}$ symmetry) normally attributed to $sp^4$-$sp^3$ bonds or C-C and C=C stretching vibrations of polylene-like structures.

Finally, a recovery of the graphitic order is observed after the reduction by heat-treatment, leading to graphitization indexes of 35.4 and 23.9 for GSM-BR and GSM-HR, respectively (Fig. 2). These results showed higher level of graphitization as compared to XRD. Most probably, Raman is possible to detect graphite with different orientation levels, depending on their origin, and that could be the source of their different $I_{D}/I_{G}$ values. This observation is influenced by the fact that we have introduced oxygenated functional groups by the harsh oxidation treatment of graphite. Then, the thermal treatment would reduce the graphite in different ways.

FE-SEM images reveal a common lamellar morphology, though with different sizes and stacking of layers (Figs. 3a–3f). It seems that the thermally expanded treatment (TEG) could strongly alter the lamellar morphology of GSM. Thus, the compacted stacking observed in GSM is replaced by buckled layers creating void spaces between layers. A close inspection of TEG sample allowed inferring an average distance between layers of 50 nm (inset in Fig. 3b). The lamellar morphology of GSM-H and GSM-B also evidences an interlayer expansion as compared to GSM. After reduction, the images reveal randomly aggregated, thin, crumpled sheets closely associated with each other. However, some isolated graphitic layers have been detected for GSM-HR and GSM-BR, exhibiting an apparent thickness of about 36 and 92 nm, respectively (Fig. 3).

The occurrence of functional groups at the carbon surface is unveiled by XPS spectroscopy. The C1s core level spectra are depicted in Fig. 4. The spectra were fitted using Gaussian-Lorentzian components. In Table II are listed the quantitative analyses of all the components in the samples and the percentage of each signal in the C 1s spectra. Thus, GSM sample exhibits a peak at 284.6 eV which is assigned to graphic carbon ($sp^2$) as the main phase, while $sp^3$ C-C bonding appears at 285.3 eV which typically overlap with the C-OH normally observed at 285.6 eV. Additional two components can be resolved at the long tail existing at high binding energies centered at 288.9 eV and 290.8 eV. These signals are attributed to O=C=O in carboxylic groups, and the shake-up satellite peaks due to $\pi^*$ tran-
while a very limited reversible capacity is delivered by cells assembled with NaClO₄ or NaPF₆ in carbonate based solvents (EC:DEC). This enhanced performance is good from the point of view of the observation of flat plateau in a safe voltage window, which is desirable for the anode side. Therefore, 1 M NaCF₃SO₃ in DGM electrolyte was chosen as the best electrolyte for further electrochemical experiments (Fig. 6 and Fig. 7). The galvanostatic profile of GSM exhibits a drop of potential from the open circuit potential until 0.9 V, and from 0.9–0.6 V is observed a plateau accounting with 48 mA h g⁻¹. Then, capacity values around 44 and 30.4 mA h g⁻¹ are delivered by a flat plateau at 0.57 V and the 0.5–0.01 V region, respectively (Fig. 6a). At the end of the first discharge the overall capacity is 131.7 mA h g⁻¹. During the subsequent charge, a reversible reaction is observed, with a coulombic efficiency of 83%. Further charge/discharge yields a similar profile with a slight shifting of 0.15 V. In order to check the rate capability of GSM sample, several experiments were recorded at different rate. Interestingly, the first reversible capacity is 94, 108.4, 102.8 and 101.7 mA h g⁻¹ for 2C, C, C/2 and C/10 rate, respectively. For slow kinetic, like at C/10, the cell tends to present a continuous capacity fade, but at fast rate the capacity is well preserved. Over 100

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**Table I.** Graphitization index, position of D and G bands and in-plane crystallite size (La) calculated from Raman.

| Sample | I_D/I_G | W_D/cm⁻¹ | W_G/cm⁻¹ | La/nm |
|--------|---------|-----------|----------|-------|
| GSM    | 17.8    | 1350      | 1582     | 89.3  |
| TEG    | 59.6    | 1352      | 1582     | 294.1 |
| GSM-H  | 0.0     | 1349      | 1583     | 4.9   |
| GSM-HR | 23.9    | 1350      | 1582     | 119.0 |
| GSM-B  | 1.8     | 1350      | 1582     | 9.1   |
| GSM-BR | 35.4    | 1351      | 1583     | 178.6 |

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**Table II.** Type and amount of functional groups determined by XPS.

| Sample | C/O | C% | Si% | S% | C(sp2) | C-OH | C-O-C | CO(OH) | π-π* |
|--------|-----|----|-----|----|--------|------|-------|--------|------|
| GSM    | 24.9| 95.4|0.8  | -  | 55.9   | 33.6 | -     | 1.4    | 9.1  |
| TEG    | 18.4| 93.8|1.1  | -  | 55.8   | 35.1 | -     | 1.5    | 7.6  |
| GSM-H  | 2.8 | 71.4|0.54 |2.2 | 17.1   | 0.6  | 49.7  | 26.5   | 6.1  |
| GSM-HR | 6.8 | 85.5|1.3  |0.7 | 42.1   | 45.9 | -     | 9      | 3    |
| GSM-B  | 11.4| 91.5|0.44 | -  | 48.9   | 38   | 2.2   | 3.3    | 7.6  |
| GSM-BR | 14.2| 92.5|1.0  | -  | 46     | 40.3 | -     | 5      | 8.7  |
cycles, an outstanding capacity retention is observed at C rate which delivered 100 mA h g\(^{-1}\), resulting a 93% of efficiency. The plateau observed in galvanostatic curves for GSM sample is very similar to that observed for a flexible polypimide graphite films reported by Han et al. but they used NaPF\(_6\) in diglyme as electrolyte.\(^{49}\) However, Zhu et al.\(^{17}\) reported the electrochemical behavior of natural graphite in NaCF\(_3\)SO\(_3\)/tetruglyme electrolyte exhibiting a shifting of the potential plateau of ca. 0.2 V as compared with our GSM sample. In turn, this shifting was only 0.15 V when using NaCF\(_3\)SO\(_3\) in diglyme.\(^{13,14}\)

The galvanostatic profile of TEG sample exhibits a flat plateau during discharge between 0.65–0.55 V and the total first discharge is 200 mA h g\(^{-1}\). This first discharge capacity is higher than for GSM sample. However, the coulombic efficiency in first cycle is 66%. The large interlayer distance allowed more Na\(^{+}\) insertion. The initial irreversible capacity is commonly ascribed to the partial reductive decomposition of the electrolyte, the formation of a solid-electrolyte interphase (SEI) layer, sodium irreversible trapping and remaining oxygen-containing groups in the interlayer of TEG. Thus, the reversible capacity for TEG is 120 mA h g\(^{-1}\) which is still higher than for GSM. The cycling experiments at several rates for TEG electrode yields 78.2, 120, 105.2 and 94.5 mA h g\(^{-1}\) for 2C, C, C/2 and C/10 rates, respectively. The best performance is recorded at C rate, being able to deliver 115 mA h g\(^{-1}\) after 100 cycles, exhibiting an efficiency of 96%. The capacity and efficiency for TEG is higher than that of original GSM over 100 cycles at C rate. The amount of remaining oxygen-containing groups in the interlayer of TEG should in principle be optimized to maintain the sufficient interlayer distance and maximize possible positions for Na-ion storage. From Raman spectra, the TEG sample exhibited higher graphitization index (59.6) and in-plane correlation length (La = 294) over all the samples. Due to this fact the higher capacity in Na-cells is observed.

The effect of partial oxidation-reduction performed by Hummer and Brodie’s modified methods on the electrochemistry is shown in Fig 7. For the sake of clarity, Fig. 7 shows the galvanostatic discharge
measured at the 2nd cycle for all the treated samples. The reversible capacity for the expanded graphite obtained by these two methods is lower than 60 mA h g\(^{-1}\). For instance, after thermal treatment at 500 and 1000 \(^\circ\)C the capacity is 55 and 38 mA h g\(^{-1}\). When an alternative reduction treatment is performed, such as with the glucose under sonication\(^{50}\) or with Fe and HCl,\(^{51}\) it is not possible to get an optimum expanded interlayer distance (Fig. S3 and S4) and consequently sodium insertion cannot be improved.

The structural changes induced by the electrochemical sodium intercalation were studied in GSM and TEG samples by recording ex situ XRD patterns. An expansion of the graphitic interlayer distance is observed during the intercalation of sodium into GSM and TEG (Figs. 8 and 9). At the beginning of the intercalation, several high stage graphite intercalation compounds will be formed (n>2). For instance, a splitting of the (002) diffraction line to lower and higher angles occurs to values of 25.4\(^\circ\) and 27.9\(^\circ\) at 0.88 V and then to 24.9\(^\circ\) and 28.6\(^\circ\) at 0.78 V. As the intercalation proceeds, stage-2 is originated at 0.7 V (Fig. 8e). Then, a transition from stage-2 to stage-1 is observed at 0.55 V (Fig. 8f). In that way, at the end of the discharge, at 0.01 V, several diffraction lines at different angles emerge which correspond to the formation of stage-1. These results are in agreement to those previously reported.\(^{16–18}\) So far, the intercalation mechanism has not been studied for thermally expanded graphites (TEG) yet. Irrespective of achieving higher capacity (ca. 15–20 mA h g\(^{-1}\)) for TEG than for GSM, similarities in the ex-situ XRD patterns are observed (Fig. 9). Upon a first discharge, a new set of (00l)
Figure 6. (a) Typical galvanostatic discharge/charge profiles of GSM sample at C rate using 1.0 M NaCF$_3$SO$_3$/DGM electrolyte. (b) Sodium storage performance versus cycle number at 2C, C, C/2 and C/10. (c) Typical galvanostatic discharge/charge profiles of TEG sample at C rate using 1.0 M NaCF$_3$SO$_3$/DGM electrolyte. (b) Sodium storage performance versus cycle number at 2C, C, C/2 and C/10.

Figure 7. (a) Effects of the oxidation induced by Hummer’s method on the electrochemical performance of GSM sample. (b) The same than (a) but after reduction. (c) Effects of the oxidation induced by Brodie’s method on the electrochemical performance of GSM sample. (d) The same than (c) but after reduction. A number of oxidized samples were obtained. They were labeled as GSM-HXT and GSM-BXT (where ‘X’ indicates the number of hours exposed to Hummer or Brodie’s method and ‘T’ the sintering temperature).

Figure 8. Ex-situ XRD patterns of GSM in sodium cell with 1M sodium triflate in diglyme recorded at different potentials: (a) pristine electrode at 3.0 V, (b) 0.88 V, (c) 0.82 V, (d) 0.78 V and relaxed all weekend, (e) 0.7 V, (f) 0.55 V and (g) at 0.01 V.
reflections appeared for TEG, which are indexed as belonging to the stage-1 of the Na\textsubscript{x}(DGM)\textsubscript{2}C\textsubscript{20} compound\textsuperscript{15,16}. Then, upon charging the initial position of the (002) reflection is retrieved, evidencing the reversibility of the insertion process. Its enhanced broadening involves a structural modification of the interlayer spacing to allow sodium diffusion. Recently, Cohn et al.\textsuperscript{51} showed stable capacity of ca. 150 mA h g\textsuperscript{−1}, suggesting a stoichiometry of Na(Diglyme)\textsubscript{x}C\textsubscript{15}, that is in agreement with previous reports on chemically derived stage 1 Na\textsuperscript{+} ternary graphite intercalation compounds (GICs).

Figure 10 shows a 1D Patterson diagram along the c-axis calculated from the XRD (00l) peak intensities. The vertical axis indicates the electron density of atoms, while the horizontal one shows the distance between atoms. Assuming an interlayer distance of 11.7 Å, it can be concluded that the Na-C distance is 5.85 Å. Also, the additional signals at intermediate values can be ascribed to the O-O, C-C and C-O bonds of the two molecules of diglyme that are co-intercalated per alkali ion\textsuperscript{52}. Therefore, we confirm that solvated sodium ions intercalate into thermally expanded graphite via a stage evolution process, forming a set of ternary graphite intercalation compounds (Fig. 11).\textsuperscript{52}

Conclusions

Among all the expanded graphites evaluated in this work, the thermally expanded graphite exhibits an improved electrochemical performance as compared to its natural graphite. The reduction of graphite oxide obtained by Brodie and Hummer’s modified methods has not provided an optimal interlayer distance to co-intercalate sodium. The thermally expanded graphite obtained by means of fast heating of graphite bisulfate at 1400 °C reached an optimal interlayer distance of 3.388 Å. This value is slightly higher than for natural graphite and would provide efficient space to co-intercalate sodium. Thus, the use of glyme-based electrolytes (sodium triflate in diglyme), which allow Na(dgm)\textsubscript{2} intercalation, resulted in higher capacities for TEG and GSM samples than using standard electrolytes. Excellent capacity retention over 100 cycles is observed for TEG and GSM which retained about 96 and 93% of the capacity, respectively. Also, the use of sodium triflate as a salt minimized the voltage polarization to 0.15 V which compared very favorable with previous studies (~0.2 V). The ex-situ XRD patterns of TEG and GSM cycled electrodes showed the progressive and reversible formation of the Na\textsubscript{x}(DGM)\textsubscript{2}C\textsubscript{20} stage 1.

Acknowledgments

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Thermally expanded graphite

Stage 2

Stage 1

Figure 11. Schematic representation of sodium storage mechanism into thermally expanded graphite electrode showing stage 2 and stage 1.

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