Graphitic carbon foams as anodes for sodium-ion batteries in glyme-based electrolytes

Jorge Rodríguez-García ^a, Ignacio Cameán ^{a,*}, Alberto Ramos ^b,
Elena Rodríguez ^a, Ana B. García ^a

^aInstituto Nacional del Carbón, CSIC, Francisco Pintado Fe 26, 33011 Oviedo, Spain

^bDepartamento de Química Inorgánica, Orgánica y Bioquímica, Instituto Regional de Investigación Científica Aplicada, Universidad de Castilla-La Mancha, Campus Universitario, 13071 Ciudad Real, Spain

ABSTRACT

The electrochemical performance as potential anodes for sodium-ion batteries of boron-doped and non-doped graphitic carbon foams is investigated by galvanostatic cycling *versus* Na/Na⁺ at different electrical current densities, in glyme-based electrolytes which are known to allow the intercalation of the Na⁺ ions into graphite. The influence of materials composition and graphitic degree on battery parameters is firstly determined and further discussed by analyzing the mechanism of the electrochemical storage of Na⁺ ions into these materials which was found to occur through different combinations of pseudocapacitive intercalation and diffusion-controlled intercalation processes. In summary, the results of this study have demonstrated that graphitic carbon foams match a very acceptable capacity with excellent cycle stability as well as performance at high electrical current densities (up to ~ 90 mAh g⁻¹ after 300 cycles at 1.9 A g⁻¹ with coulombic efficiency ~ 100 %) which make them suitable for sodium-ion battery applications. Overall, the increase of the interlayer spacing between the graphene layers and the presence of boron promote the pseudocapacitive intercalation which is responsible for the remarkable rate performance of these materials, whereas the improvement of diffusion-controlled intercalation capacity is mainly related to larger boron content.

Keywords: Sodium-ion battery; Graphitic carbon foam anode; Glyme-based electrolyte; Sodium storage mechanism; High-rate capability

* Corresponding author

E-mail address: icamean@incar.csic.es

1. Introduction

Sodium-ion batteries (SIBs) were developed alongside lithium-ion batteries (LIBs) in the 1970s and 1980s [1-3], but afterwards they were completely overshadowed by the commercial success of LIBs owing to their higher energy density. However, the natural abundance of sodium (4th most abundant element on earth) as well as its lower cost and environmental awareness as compared with lithium [4], have made SIBs an attractive alternative to LIBs, particularly for large-scale electrical energy storage (EES) systems which are made up of a great number of batteries.

Research on SIBs has grown exponentially since 2010 and it has benefited from the maturity reached after 30 years of R&D on LIBs, specifically in the field of cathodic materials since several of them are drawn up replacing lithium by sodium in the analogue compound such as transition-metal oxides (layered oxides, tunnel oxides) and polyanionic compounds (phosphates, pyrophosphates, fluorophosphates), with promising results in some instances [5-11]. Likewise, the electrolyte formulations tested for these batteries consist mainly of sodium salts dissolved in organic carbonates mixtures [12,13], some also including ionic liquids (hybrid electrolytes) [14]. In contrast, the development of anodic materials for SIBs has been somewhat more limited, especially regarding carbon-based materials [15-17], since sodium hardly intercalates into graphite - the anode of choice *par excellence* in LIBs - to form binary graphite intercalation compounds (b-GIC). Therefore, only b-GIC of the formula NaC_{64} were obtained in low current density experiments for electrochemical intercalation of Na^+ ions in graphite [3], amounting to a reversible capacity of $\sim 35 \text{ mAh g}^{-1}$, which contrasts with the LiC_6 intercalation

1 compound attained for Li^+ ions (theoretical capacity of 372 mAh g^{-1}). This
2 limitation has been assumed to be the result of the stress induced in the
3 graphite structure by Na^+ ions intercalation, and the ionic radius of Na^+ ion,
4 which is $\sim 0.3 \text{ \AA}$ larger than that of Li^+ ion [18]. Interestingly, it has been recently
5 circumvented in part by using ether-based electrolytes which allow the
6 electrochemical co-intercalation of solvent molecules along with the Na^+ ions to
7 form ternary graphite intercalation compounds (t-GIC) in a highly reversible
8 process. Taking advantage of this co-intercalation phenomena which was firstly
9 applied to SIBs using a diglyme-based electrolyte by Jache and Adelhem [19],
10 reversible capacities in the range $100\text{-}150 \text{ mAh g}^{-1}$ with coulombic efficiency
11 and capacity retention approaching 100 % as well as excellent rate capability
12 were reported for graphite anodes [20-23]. First of all, these findings have
13 demonstrated that, in contrast to the general belief, graphite is a promising
14 anode material for SIBs. In addition, they are interesting enough to explore the
15 impact on battery performance of different electrolyte solvents able to form t-
16 GIC [22, 24] as well as graphitic materials other than *stricto sensu* graphite that,
17 to the best of our knowledge, have not been studied previously.

41 Carbon foams (CFs) are lightweight materials with high mechanical
42 strength, high temperature tolerance, low thermal expansion coefficient and
43 tailorable thermal and electrical conductivities which make them suitable for
44 several applications, including active materials for electrodes of energy storage
45 devices, particularly after graphitization by heat treatment at high temperature
46 [25]. Different carbon materials can be used as precursors for the manufacture
47 of graphitic carbon foams (GCFs), such as polymers, mesophase pitches and
48 coals [25]. Among them, coals are an economical alternative because, in
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

addition to availability, the carbon foam production does not require any previous precursor preparation, foaming agents or stabilization steps [26]. Coal-based carbon foams with different properties were prepared by a simple coal carbonization process by adjusting both operating conditions (temperature and pressure) and coal plastic behavior. A subsequent heat treatment at high temperature (≥ 2400 °C), in an inert atmosphere, was reported to achieve their transformation into graphitic foams with very high degree of three-dimensional structural order, particularly in the presence of boron [27]. Thus, GCFs with crystalline parameter values ($d_{002} \sim 0.3365$ nm, $L_c \sim 41$ nm, $L_a \sim 68$ nm) and porosity ($S_{\text{BET}} \sim 4$ m² g⁻¹) comparable to oil-derived synthetic graphite, which is massively used as anode in commercial LIBs, were prepared. In this context, several boron-doped and non-doped coal-based GCFs were successfully applied as active materials in the anodes of these batteries [28].

With these precedents in mind, the electrochemical performance as potential anodes in SIBs of several boron-doped and non-doped GCFs that were prepared from a bituminous coal [27, 28] is herein investigated by galvanostatic cycling at constant and variable electrical current density, using two glyme-based electrolytes, namely sodium triflate (sodium trifluoromethanesulfonate, NaOTf) in diglyme (diethylene glycol dimethyl ether, DG) or in tetraglyme (tetraethylene glycol dimethyl ether, TTG). The results are discussed in terms of battery reversible capacity, irreversible capacity in the first cycle, capacity retention along cycling and cycle efficiency by considering the influence of GCFs composition and graphitic degree as well as of electrolyte solvent properties. The mechanism of interaction of Na⁺ ions with GCFs is also analyzed through cyclic voltammetry experiments at different sweep rates,

1 following a method which is based on the dependence between peaks currents
2 and scan rates [29]. By this method, the contributions of diffusion-controlled
3 intercalation and capacitive Na^+ reactions, which were reported to occur during
4 sodium electrochemical storage in natural graphite [23], to the total sodiation
5 capacity of GCFs electrodes are quantified and related to both composition and
6 graphitic degree.
7
8
9
10
11
12
13
14
15

16 **2. Materials and methods**

17 *2.1. Graphitic carbon foams: preparation and structural/textural* 18 *characterization* 19 20 21 22 23 24 25 26

27
28 A low volatile bituminous coal from USA (Litwak) was selected as the
29 precursor of the carbon foams. Characterization data of the coal is reported
30 elsewhere [27]. Boron oxide (B_2O_3) was used as boron source. The carbon
31 foams (boron-doped and non-doped) were prepared by a two-stage procedure
32 and further heat treated in the temperature interval 2400-2800 °C for 1 h in
33 argon flow, by using a graphite electrical furnace. The experimental set-up can
34 be found in [27, 28]. The graphitized boron-doped carbon foams were identified
35 by the initial boron loading (5B or 10B wt.%), and the treatment temperature (24
36 for 2400 °C, 26 for 2600 °C, etc.), such as 5B24. Correspondingly, the non-
37 doped graphitized carbon foams were named 0B24, 0B26 or 0B28. Besides
38 these, another non-doped graphitic carbon foam, denoted MCF28, was
39 obtained from one commercial mesophase-based carbon foam by heat
40 treatment at 2800 °C.
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

1 Boron contents in the GCFs were determined by inductively coupled
2 plasma (ICP) mass spectrometry. The samples were firstly digested by fusing
3 with sodium peroxide and then dissolved in water together with a small amount
4 of hydrochloric acid. The boron in the solutions was analyzed by standard
5 additions.
6
7
8
9
10

11 The interlayer spacing, d_{002} , and the mean crystallite sizes along a , L_a , and
12 c , L_c , axes are used to evaluate the degree of graphitic structural order of the
13 carbon foams [30]. They were calculated from the X-ray diffractograms which
14 were recorded in a Bruker D8 powder diffractometer as described elsewhere
15 [31]. The d_{002} was determined from the position of the (002) peak by applying
16 Bragg's equation while the L_c and L_a were calculated from (002) and (110)
17 peaks, respectively, using the Scherrer formula, with values of $K = 0.9$ for L_c
18 and $K = 1.84$ for L_a [32]. The broadening of diffraction peaks due to instrumental
19 factors was corrected with the use of silicon standard. Typical standard errors of
20 the XRD parameters are $< 3 \%$ and $< 8 \%$ of the reported values for L_c and L_a ,
21 respectively; the interlayer spacing values are more precise, with standard
22 errors of $< 0.03 \%$.
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42

43 The textural properties of the carbon foams were measured by N_2
44 adsorption-desorption at $-196 \text{ }^\circ\text{C}$ in a Micromeritics ASAP 2420 volumetric
45 adsorption system. Before measurements, the samples were degassed
46 overnight at $200 \text{ }^\circ\text{C}$. The specific surface areas (S_{BET}) were calculated by
47 applying the Brunauer–Emmett–Teller (BET) method, taking 0.162 nm^2 for the
48 cross-sectional area of the nitrogen-adsorbed molecule. Total pore volumes (V_t)
49 were determined by the amount of N_2 adsorbed at $p/p^\circ = 0.985$. Micropore
50 volume ($< 2 \text{ nm}$) was calculated from the Dubinin-Radushkevich equation [33].
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

2.2. *Electrolytes: preparation and conductivity/viscosity measurements*

Two electrolytes consisting in 1 M solutions of sodium triflate (sodium trifluoromethanesulfonate, NaOTf), supplied by Aldrich, in diglyme (diethylene glycol dimethyl ether, DG) or in tetraglyme (tetraethylene glycol dimethyl ether, TTG) were prepared in a glove box under argon atmosphere, with oxygen and water contents below 0.1 ppm, by magnetic stirring. Solvents were also provided by Aldrich (99.5 % DG, 99.0 % TTG) and used as received.

The ionic conductivity of the glyme-based electrolytes was measured in the glove box using an XS COND70 conductivity portable meter equipped with a VPT80/1 cell. A HAAKE rotational Viscotester VT5 R was used to measure their viscosities. By this procedure, a disk/spindle is submerged in the solution and the force which is necessary to overcome the resistance of the viscosity to the rotation is measured. The viscosity value in mPa s is automatically calculated by the instrument on the basis of the speed and the geometry of the spindle. According to preliminary tests, a R1 spindle was selected and the measurements were carried out at increasing speeds (up to 200 rpm) from which an average viscosity value was determined.

2.3. *Cell preparation and electrochemical measurements*

Two-electrode (working + counter) and three-electrode (working + counter + reference) Swagelok-type cells were used for the electrochemical measurements of the GCFs. In the two-electrode configuration, the working

1 electrode (WE) was prepared from the slurry formed by adding the
2 corresponding GCFs (active material, 92 wt.%) to a solution of polyvinylidene
3 fluoride (PVDF, binder, 8 wt.%) in 1-methyl-2-pyrrolidone (NMP) and stirring
4 vigorously for over 20 h. Afterwards, a drop of the slurry was spread on a
5 copper foil of 12 mm of diameter and 25 μm of thickness which was
6 subsequently dried under vacuum at 120 $^{\circ}\text{C}$ for 2 h and, finally, hydraulically
7 pressed at ~ 40 MPa. The electrode load (active material + binder) was
8 calculated by weight difference, being in the range 1.1 – 6.5 mg cm^{-2} . A metallic
9 sodium disc of 12 mm of diameter was used as counter electrode (CE). For the
10 three-electrode cell, an additional sodium disc was used as reference electrode
11 (RE). Three-electrode cells with RE and CE of metallic sodium, and a stainless-
12 steel cylinder as WE were also used for the electrochemical characterization of
13 the electrolytes. The electrodes were separated from each other by micro-fiber
14 glass discs impregnated with a few drops of the electrolyte. Cell assemblage
15 was carried out in a dry box under argon atmosphere with water and oxygen
16 contents below 0.1 ppm. The initial cell potential was always in the range 2.7-
17 3.0 V vs Na/Na $^{+}$.
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40

41 The electrochemical measurements of GCFs cells were conducted in a
42 Biologic multichannel VMP2/Z potentiostat/galvanostat. Galvanostatic cycling of
43 two-electrode cells was performed in the 0.003-3.0 V potential range vs Na/Na $^{+}$
44 at constant (37.2, 372.0 and 1860.0 mA g^{-1} for at least 50 cycles) or variable
45 (from 37.2 to 744 mA g^{-1} , 10 cycles each current, starting and finishing at the
46 lowest one) electrical current densities. Prolonged cycling (300 cycles) at 372.0
47 and 1860.0 mA g^{-1} was also conducted with some electrodes. The cyclic
48 voltammograms (CV) of the three-electrode cells were collected in the 0.003-2.5
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

1 V vs Na/Na⁺ potential range for 3 cycles at different scan rates, from 0.2 to 3.0
2 mV s⁻¹.
3
4

5 Cyclic voltammetry (CV) experiments of the electrolyte three-electrode
6 cells were carried out for 3 cycles at a scan rate of 50 mV s⁻¹ between two
7 potentials close to 3.0 V vs Na/Na⁺ (cell initial potential value). Subsequently,
8 the potential range was progressively extended to observe oxidation and/or
9 reduction peaks. Once the electrolyte potential window was identified, CV
10 measurements were repeated, at 0.2 mV s⁻¹ for 3 cycles, between potential
11 limits at which the oxidation and reduction processes were observed to obtain
12 better-defined profiles.
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27

28 **3. Results and discussion**

29 **3.1. Galvanostatic cycling of graphitic carbon foams electrodes**

30
31
32
33
34
35
36
37
38 The specific discharge (C_{disc}) and charge (C_{charge}) capacities in the 1st, 2nd
39 and 50th, cycles, irreversible capacity in the 1st discharge-charge cycle (C_{irr}) and
40 capacity retention (R) parameters determined from the galvanostic cycling of
41 GCFs electrodes against sodium in 1M NaOTf in diglyme (NaOTf/DG) and in
42 1M NaOTf in tetraglyme (NaOTf/TTG) electrolytes, at an applied electrical
43 current density of 37.2 mA g⁻¹, are summarized in Table 1. First of all, it can be
44 concluded that the use of these electrolytes allows the insertion/de-insertion of
45 sodium ions (according to the proposed mechanism, Na⁺ solvated species [19])
46 into GCFs anodes as shown by the reversible capacities. Maximum values of
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

1 this electrochemical parameter around 100 mAh g⁻¹ after 50 cycles, which are
2 somewhat in the order of some reported for different anodic non-graphitic
3 carbon materials in typical electrolytes (sodium salts dissolved in organic
4 carbonates mixtures) [6-12, 34], were reached in this work. GCFs electrodes
5 also exhibit good stability along cycling with discharge and charge capacities
6 retentions in the ranges 77-92 % and 83-98 %, respectively (Table 1). Focusing
7 on the values of the irreversible capacities (irreversible consumption of Na⁺) in
8 the first discharge-charge cycle in Table 1 (20-61 %), they are larger than
9 expected since the use of glyme-based electrolytes in SIBs has been found to
10 suppress electrolyte decomposition compared to carbonate-based electrolytes,
11 thus resulting in the formation of a negligible SEI film on the surface of graphite
12 electrodes [19-23]. SEI formation on carbon anodes in SIBs using sodium salts
13 dissolved in organic carbonates mixtures is usually proportional to the surface
14 area of the active carbon material [16]. However, *a priori*, this effect does not
15 appear applicable for GCFs electrodes, despite the fact that GCFs materials
16 show mostly very low porosity (Table 2). In any event, the lowest C_{irr} values in
17 this work for 0B28, 5B28 and MCF28 electrodes are only marginally higher than
18 those reported for graphite electrodes in similar conditions [22]. Finally, it should
19 be noted that the cycle efficiency increases rapidly along cycling for all GCFs
20 electrodes, being 80-95 % in the 2nd cycle and 92-100 % by the end of cycling.

21 As regards the influence of the electrolyte on the electrochemical
22 performance of GCFs electrodes against sodium at low electrical current
23 density (37.2 mA g⁻¹), overall the results are better in NaOTf/DG than in
24 NaOTf/TTG electrolytes (Table 1), particularly, the reversible capacity. A similar
25 tendency has been previously reported by other authors for commercial

graphite electrodes in SIBs using linear glymes with different chain length [22]. Provided that the two electrolytes used in this work are electrochemically stable (no red-ox processes are observed in the cyclic voltammograms of the electrolytes three-electrode cells in Fig. S1 of Supporting Information) in the potential range (0.003-3 V vs Na/Na⁺) at which GCFs electrodes were cycled this difference can be, among other factors, attributed to the lower viscosity as well as higher ionic conductivity of NaOTf/DG (21 mPa s; 3110 $\mu\text{S cm}^{-1}$) in comparison with NaOTf/TTG (32 mPa s; 1392 $\mu\text{S cm}^{-1}$). Good ionic conductivity and low viscosity to improve the ion mobility are electrolyte crucial properties for correct battery operation. In line with this, discharge capacities of 77 mAh g⁻¹ vs only 24 mAh g⁻¹ were calculated for 0B28 electrode at the end of cycling in NaOTf/DG and NaOTf/TTG electrolytes, respectively, with comparable capacity retention (Table 1). This difference is more modest for 0B26, 5B24, and 5B28 electrodes and even negligible for both 10B24 and mesophase-based MCF28. In contrast, the capacity delivered by 0B24 is slightly larger by using NaOTf/TTG electrolyte. Therefore, it appears that the graphitic carbon foam used as active material in the electrode determines the significance of the electrolyte influence. As an example, the specific discharge (sodiation) capacities vs cycle number plots of GFCs electrodes are shown in Fig. 1. In general, larger discharge capacities along cycling were measured for non-doped GFCs materials with higher interlayer distance d_{002} (Table 2, Fig. 1a). Thus, values of 103, 77 and 58 mAh g⁻¹ were determined for 0B24 (d_{002} 0.3379 nm), 0B28 (d_{002} 0.3373 nm) and MCF28 (d_{002} 0.3366 nm), respectively, in NaOTf/DG after 50 discharge-charge cycles. This finding suggests that the scope of the electrochemical insertion of glyme-solvated Na⁺ ions relies mainly

on the available space between the graphene layers with glyme solvent playing a secondary role. However, this does not apply at all for boron-doped GCFs (Table 2, Fig. 1b) given that these materials with interlayer distances in the range from 0.3365 to 0.3354 nm show discharge capacities along cycling basically comparable. Moreover, the performance as anodes of boron-doped GCFs (e.g. 5B24, 5B28 and 10B24 in NaOTf/DG) compares well with that of the best non-doped GCFs (e.g. 0B24 in NaOTf/DG). According to the work of Yamada et al. [35], boron-doped graphite-like layered materials may provide higher reversible capacity than graphite in SIBs because of the electron deficiency of the boron atom decreases the energy level in the bottom of the conduction band, thus improving the materials electron affinity. In summary, it seems that the presence of boron as well as the graphene interlayer distance control the galvanostatic cycling of GCFs electrodes against metallic sodium in different glyme-based electrolytes.

3.2. Electrochemical storage of glyme-solvated Na⁺ ions into the graphitic carbon foams: potential and mechanism

In order to gain further insight into the interaction of the glyme-solvated Na⁺ ions with the graphitic carbon foams during the galvanostatic process, the potential (E) vs Na/Na⁺ against discharge/charge specific capacities plots for cycles 1, 2, 25 and 50 (potential profiles) of GCFs electrodes in both electrolytes are herein discussed. Since these profiles were very similar for a given type of GFCs (non-doped or boron-doped) electrodes provided the same electrolyte solvent (DG or TTG), only 0B28 and 5B28 (Fig. 2) will be

commented in detail, whereas those of 0B24, 0B26, 5B24, 10B28 and MCF28 electrodes are included in Fig. S2 of Supporting Information. All of these profiles comprise mainly three regions, namely in descending order of potential, a more or less sloping plateau, a basically flat plateau and a sloping curve. Focusing on the discharge curves, it can be observed that the potential vs Na^+/Na drops quickly to the point at which the sodiation process begins with no slope differences between the first and the following cycles. That is, the decomposition of the glyme-based electrolytes on the surface of the GCFs electrodes during the first discharge cycle to form the SEI film is insignificant, as reported previously for graphite electrodes [19-23], and therefore, does not account for the irreversible capacities (irreversible consumption of Na^+ in the first discharge-charge cycle) calculated for these electrodes (Table 1). Regarding the sodium storage potential, GCFs electrodes show larger values in the TTG-based electrolyte. These differences can be better appreciated in the differential capacity plots (Fig. 2). Thus, potentials of 0.65-1.10 (range of sloping plateau), 0.60 (flat plateau) and 0.15 (sloping curve) V vs Na/Na^+ were calculated for the three sodiation regions of 0B28 electrode in NaOTf/DG against values of 0.75-1.25, 0.7 and 0.20 V vs Na/Na^+ , respectively, in NaOTf/TTG. This trend is consistent with a recent study on the impact of glymes as electrolyte solvents for graphite co-intercalation electrodes in SIBs [22], which concluded that the redox potentials of graphite sodiation and desodiation systematically increase as the glyme chain length increases provided a linear structure of the later. Potential redox shifts similar to the values calculated in this work for GCFs electrodes were reported in this study using the same glyme-based electrolytes. According to Kim et al. [24], this fact is

1 attributable to the stronger screening effect for the repulsion between Na⁺ ions
2 with longer chain solvent species, which increases the sodium storage potential.
3
4 Furthermore, the presence of boron in the GCFs electrodes leads to an
5 additional potential shift to higher values. This is related to the above mentioned
6 larger electron affinity of the boron-doped graphitic materials [35]. As an
7 example, potentials of 0.75 and 0.87 V were measured for the sodiation (flat
8 plateau) of 5B28 in NaOTf/DG and NaOTf/TTG electrolytes, respectively (Fig.
9 2).

10
11
12
13
14
15
16
17
18
19
20 Considering the results discussed so far in this section, it seems obvious
21 that the sodium storage mechanism depends on the potential region. To
22 investigate this mechanism, cyclic voltammetry (CV) data of GCFs electrodes at
23 different scan rates, from 0.2 to 3 mV s⁻¹, were analyzed on the basis of the
24 equation $i = a \nu^b$. In this equation, the measured current i (A) obeys a power
25 law relationship with the scan rate ν (mV s⁻¹), whereas a and b are adjustable
26 parameters. The b parameter is the slope of the linear line obtained by plotting
27 $\log i$ vs $\log \nu$, and its value (in the interval 0.5–1.0) depends on the current
28 origin (intercalation or capacitive processes) [23, 29, 36]. Thus, a b value of 0.5
29 indicates that the current comes primarily from a diffusion-controlled sodium
30 intercalation, whereas for a value of 1.0 the current is predominantly capacitive
31 (surface-limited). As an example, the second cycle voltammograms of 0B28 in
32 NaOTf/DG, at various scan rates, and the corresponding b values determination
33 for the cathodic peaks (sodiation) labelled 1, 2, 3, 4 and 5 are displayed in Fig.
34 3 (CV profiles of other GCFs electrodes are provided in Fig. S3 of Supporting
35 Information). For this electrode, b values were in the range 0.7-0.9 suggesting
36 different combinations of intercalation and capacitive mechanisms of sodium
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

storage (Fig. 3b). The b data of some GCFs electrodes are plotted as a function of potential vs Na/Na⁺ for cathodic (sodiation) peaks (from CVs at the scan rate of 0.2 mV s⁻¹) in Fig. 4. At potentials higher than ~ 0.8 V, the sodiation of non-doped 0B24 and 0B26 occurs primarily by a capacitive process (b close to 1), whereas some contribution of intercalation to the measured current appears obviously for 0B28 ($b \sim 0.8$). Unlike these, the mesophase-based MCF28 shows a predominant sodium intercalation process at potential of ~ 1.0 V ($b \sim 0.6$). At low potentials, different combinations of capacitive and intercalation reactions can be inferred for all non-doped GCFs (Fig. 4a). As regards boron-doped GCFs electrodes, a similar sodiation mechanism dependency on the potential was observed (Fig. 4b). Therefore, a considerable amount of the cathodic current measured for GCFs electrodes comes from a capacitive (surface-limited) sodiation process. However, considering the graphitic structure and very low surface area of GCFs materials (Table 2), this capacitive current can be mainly ascribed to a pseudocapacitive intercalation process which arises from the intercalation of ions (solvated Na⁺ ions in this work) into the layers or tunnels of a redox-active material accompanied by a faradaic charge-transfer with no crystallographic phase change, since the other possible capacitive storage mechanism, the so-called redox pseudocapacitance is related with the adsorption of ions on material surface or near-surface [20, 37]. Consequently, the total current response of GCFs electrodes is a combination in different proportions of pseudocapacitive intercalation (CI) and diffusion-controlled intercalation (DCI) currents. The quantitative contribution of these two currents were calculated on the basis of the dependence between peak currents and voltammograms scan rate according to the equation $i = k_1 v + k_2 v^{1/2}$ ($i/v^{1/2} = k_1$

$v^{1/2} + k_2$, for analytical purposes) in which i (A) is the current at a given potential, v (mV s^{-1}) is the scan rate, and k_1 and k_2 are constants [23, 29, 36, 37]. In this equation, $k_1 v$ and $k_2 v^{1/2}$ correspond to CI and DCI currents, respectively, and thus they can be calculated by determining the constants. Following the former equation, the scan rate dependence of the current for the cathodic peaks (sodiation) 1, 2, 3, 4 and 5 (see Fig. 3) of 0B28 in NaOTf/DG is plotted in Fig. 5a. As seen, there is a linear relationship from which the slope k_1 and the y-axis intercept point of a straight line k_2 can be determined for a given current peak. The calculated CI and DCI current contributions to the total measured current for each cathodic peak of this material are consistent with b data in Fig. 4a (red line). Thus, DCI currents (66-69 %) are moderately dominant at low potentials (< 0.8 V; $b \sim 0.7$), whereas the contributions of both CI and DCI currents appear comparable at high potentials ($b \sim 0.8$). Accordingly, the capacitive and diffusion-controlled intercalation contributions to the total measured cathodic current in a typical CV at the scan rate of 0.2 mV s^{-1} were calculated (Fig. 5b). By comparing the shaded area with the total storage charge in the sodiation of 0B28 in NaOTf/DG, it can be said that about 41 % comes from a capacitive process (see data of other CGFs electrodes in Tables S1 and S2 of Supporting Information). The corresponding capacity (gravimetrically normalized) as well as the amounts attributed to capacitive intercalation and diffusion-controlled intercalation processes for a selection of GCFs electrodes in NaOTf/DG were calculated and they are shown in Figure 6. A comparative analysis of these electrochemical results and the materials characterization data in Table 2 allow to conclude that the discharge capacity increases as the non-doped GCFs interlayer distance, d_{002} , increases. Thus, sodiation capacities of 76, 60, 61 and

46 mAh g⁻¹ were determined for 0B24, 0B26, 0B28 and MCF28 with d₀₀₂ values of 0.3379, 0.3377, 0.3373 and 0.3366 nm, respectively. As seen, this increase is mainly related to the improvement of the pseudocapacitive intercalation which grows from 20 mAh g⁻¹ for MCF28 to 50 mAh g⁻¹ for 0B24; whereas the variation of the capacity due to diffusion-controlled intercalation is more modest (26-36 mAh g⁻¹). It is therefore evident that the increase of the available space between GCFs layers promotes the intercalation of the Na⁺ ions by a pseudocapacitive process which is not limited by solid-state diffusion. Furthermore, for a similar (002) interlayer spacing, the presence of boron in the GCFs also leads to larger capacity (i. e. 5B24 and 5B28 vs MCF28, Fig. 6, Table 2). This effect is particularly remarkable in 5B24 material with larger boron content since both types of Na⁺ ions intercalations are improved. Finally, the analysis of the dependence between peak currents and voltammograms scan rate was applied to the first cycle CVs of 0B28 in NaOTf/DG (see Tables S1, S2 in Supporting Information) to discern the origin of the irreversible capacity (Table 1) since, as mentioned above, no apparent decomposition of the glyme-based electrolytes on the surface of the GCFs to account for this capacity loss was observed in the potential profiles (Fig. 2). Based on the results obtained, it appears to arise substantially from a diffusion-limited intercalation current loss which decreases from a contribution of 68 % to the total storage charge in the first sodiation cycle (Table S2) to 59 % in the second cycle (Fig. 5).

3.3. Effect of electrical current density on galvanostatic cycling of graphitic carbon foams electrodes

The cycling behavior of non-doped (0B24, 0B28, MCF28) and boron-doped (5B24, 5B28) GCFs electrodes in NaOTf/DG as well as that of 5B24 in NaOTf/TTG at increasing electrical current density (from 37.2 and 744.0 mA g⁻¹) is depicted in Fig. 7. As seen, the increase of the current density has little repercussion on the specific capacity delivered by these GCFs electrodes. Consequently, specific capacity values up to 100 mAh g⁻¹ were reached at even the highest current density of 744 mA g⁻¹ (e.g. 5B28/DG) which essentially means that these electrodes are able to basically keep their capacity after increasing twenty times the applied current density. Furthermore, all of them show stable capacities in the whole range of current densities applied, with capacity retention values over 90 %, excellent cycle efficiencies (charge capacity/discharge capacity > 98 %) and no degradation after cycling at high current densities as shown by the recovery (over 93 %) of the initial capacity at 37.2 mA g⁻¹ when returning to these conditions. This remarkable rate performance, which is hardly shown by carbon materials as SIBs anodes in organic carbonates solvent-based electrolytes [6, 9, 11, 34, 38-40], can be mainly attributed to the intercalation of the solvated Na⁺ ions by the pseudocapacitive mechanism that improves their transportability through the graphene layers.

Prolonged galvanostatic cycling experiments at high current densities (300 cycles at 0.4 and 1.9 A g⁻¹) were conducted for the non-doped 0B24 and the

boron-doped 5B24 electrodes in NaOTf/DG electrolyte. The plots of the discharge capacity against the cycle number are reported in Fig. 8. As expected from the above discussed results, both electrodes exhibit excellent capacity retention ($\geq 87\%$) as well as coulombic efficiency ($\sim 100\%$). Consequently, they are able to deliver specific capacities in the range 80-90 mAh g⁻¹ (87- 95 % of the initial capacity) after 300 cycles at the highest current of 1.9 A g⁻¹.

Overall, the rate capability of the GFCs electrodes in SIBs is comparable to that previously reported for industrial powder graphite in different glyme-based electrolytes [19, 20-23]. However, it should be noticed that regarding high cycling currents (≥ 372 mAh g⁻¹), GCFs electrodes have shown a sodiation capacity somewhat larger than graphite electrodes in the same electrolyte composition [19, 22].

4. Conclusions

The results of this study have demonstrated that graphitic carbon foams, which have been prepared from a bituminous coal by a simple procedure, are suitable anode materials for sodium-ion batteries in glyme-based electrolytes. These graphitic materials match a very acceptable capacity with excellent cycle stability as well as performance at high electrical current densities (up to ~ 90 mAh g⁻¹ after 300 cycles at 1.9 A g⁻¹ with coulombic efficiency $\sim 100\%$) which make them attractive for sodium-ion battery applications.

The electrochemical storage of glyme-solvated Na⁺ ions into the graphitic carbon foams occurs through different combinations of pseudocapacitive intercalation and diffusion-controlled intercalation processes, the former being

1 responsible for the remarkable rate performance of these carbon materials,
2 hence tackling the problem of the poor transportability of the Na⁺ ions through
3 the graphene layers. The graphitic carbon foams structure and composition
4 control the contributions of the two processes to the total stored charge, and
5 therefore, the electrode capacity. Overall, the increase of the interlayer spacing
6 between the graphene layers and the presence of boron were found to promote
7 the pseudocapacitive intercalation whereas the improvement of diffusion-
8 controlled intercalation capacity was mainly related to larger boron content. In
9 conclusion, better electrochemical performance could be achieved by preparing
10 boron-doped graphitic carbon foams with relatively large values of interlayer
11 spacing.
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30

31 Acknowledgements

32
33
34
35
36

37 Financial support from the Spanish Ministry of Economy and
38 Competitiveness MINECO (under Project ENE2014-52189-C2-2-R) and
39 Iberdrola Spain Foundation (www.fundacioniberdrola.org, Projects 2016-2017)
40 is gratefully acknowledged. J. Rodríguez-García thanks the MINECO for a
41 Ph.D. grant (FPI BES 2015-071293) to develop the work. Thanks are also given
42 to R. García of the INCAR (CSIC) for providing carbon foams.
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

References

- [1] M.S. Whittingham, Chemistry of intercalation compounds: metal guests in chalcogenide hosts, *Prog. Solid State Chem.* 12 (1978) 41-99.
- [2] K.M. Abraham, Intercalation positive electrodes for rechargeable sodium cells, *Solid State Ionics* 7 (1982) 199-212.
- [3] P. Ge, M. Foulletier, *Solid State Ionics* 28 (1988) 1172-1175.
- [4] M.D. Slater, D. Kim, E. Lee, C.S. Johnson, Sodium-Ion Batteries, *Adv. Funct. Mat.* 23 (2013) 947-958.
- [5] N. Yabuuchi, K. Kubota, M. Dahbi, S. Komaba, Research development on sodium-ion batteries, *Chem. Rev.* 114 (2014) 11636-11682.
- [6] L. P. Wang, L. Yu, X. Wang, M. Seinivasan, Z.J. Xu, Recent developments in electrode materials for sodium-ion batteries *J. Mat. Chem. A* 3 (2015) 9353-9378.
- [7] D. Kundu, E. Talaie, V. Duffort, L.F. Nazar, The emerging chemistry of sodium ion batteries for electrochemical energy storage, *Angew. Chem. Int. Ed.* 54 (2015) 3431-3448.
- [8] H.L. Pan, Y.S. Hu, and L.Q. Chen, Room-temperature stationary sodium-ion batteries for large-scale electric energy storage, *Energy Environ. Sci.* 6 (2013) 2338-2360.
- [9] V. Palomares, M. Casas-Cabanas, E. Castillo Mat3n3ez, M.H. Han, T. Rojo, Update on Na-based battery materials. A growing research path, *Energy Environ. Sci.* 6 (2013) 2312-2337.

- [10] S.W. Kim, D.H. Seo, X. Ma, G. Ceder, K. Kang, Electrode materials for rechargeable sodium-ion batteries: potential alternatives to current lithium-ion batteries, *Adv. Energy Mat.* 2 (2012) 710-721.
- [11] Y. Li, Y. Lu, C. Zhao, Y.-S. Hu, M.-M. Titirici, H. Li, X. Huang, L. Chen, Recent advances of electrode materials for low-cost sodium batteries towards practical application for grid energy storage, *Energy Storage Materials* 7 (2017) 130-151.
- [12] A. Ponrouch, E. Marchante, M. Courty, J.-M. Tarascon, M.R. Palacin, In search of an optimized electrolyte for Na-ion battery, *Energy Environ. Sci.* 5 (2012) 8572-8583.
- [13] A. Bhide, J. Hofmann, A.K. Durr, J. Janek, P. Adelhelm, Electrochemical stability of non-aqueous electrolytes for sodium-ion batteries and their compatibility with $\text{Na}_{0.7}\text{CoO}_2$, *Phys. Chem. Chem. Phys.* 16 (2014) 1987-1989.
- [14] D. Monti, A. Ponrouch, M. R. Palacin, P. Johansson, Towards safer sodium-ion batteries via organic solvent/ionic liquid based hybrid electrolytes, *J. Power Sources* 324 (2016) 712-721.
- [15] M.-S. Balogun, Y. Luo, W. Qie, P. Liu, Y. Tong, A review of carbon materials and their composites with alloy metals for sodium ion battery anodes, *Carbon* 98 (2016) 162-178.
- [16] C. Bommier, X. Ji, Recent development on anodes for Na-ion batteries, *Isr. J. Chem.* 55 (2015) 486-507.
- [17] M. Dahbi, N. Yabuuchi, K. Kubota, K. Tokiwa, S. Komaba, Negative electrodes for Na-ion batteries, *Phys. Chem. Chem. Phys.* 16 (2014) 15007-15028.

- 1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
- [18] K. Nobuhara, H. Nakayama, M. Nose, S. Nakashini, H. Iba, First-principles study of alkali metal-graphite intercalation compounds, *J. Power Sources* 243 (2013) 585-587.
- [19] B. Jache, P. Adelhem, Use of graphite as a highly reversible electrode with superior cycle life for sodium-ion batteries by making use of co-intercalation phenomena, *Angew. Chem. Int. Ed.* 53 (2014) 10169-10173.
- [20] Z. Zhu, F. Cheng, Z. Hu, Z. Niu, J. Chen, Highly stable and ultrafast electrode reaction of graphite for sodium ion batteries, *J. Power Sources* 293 (2015) 626-634.
- [21] I. Hasa, X. Dou, D. Buchholz, Y. Shao-Horn, J. Hassoun, S. Passerini, B. Scrosati, A sodium-ion battery exploiting layered oxide cathode, graphite anode and glyme-based electrolyte, *J. Power Sources* 310 (2016) 26-31.
- [22] B. Jache, J.O. Binder, T. Abe, P. Adelhelm, A comparative study on the impact of different glymes and their derivatives as electrolyte solvents for graphite co-intercalation electrodes in lithium-ion and sodium-ion batteries. *Phys. Chem.Chem. Phys.* 18 (2016) 14299-14316.
- [23] H. Kim, J. Hong, Y.-U. Park, J. Kim, I. Hwang, K. Kang, Sodium storage behavior in natural graphite using ether-based electrolyte systems, *Adv. Funct. Mat.* 25 (2015) 534-541.
- [24] H. Kim, J. Hong, G. Yoon, H. Kim, K.-Y. Park, M.-S. Park, W.-S. Yoon, K. Kang, Sodium intercalation chemistry in graphite, *Energy Environ. Sci.* 8 (2015) 2963-2969.
- [25] M. Inagaki, J. Qiu, Q.G. Guo, Carbon foams: preparation and application, *Carbon* 87 (2015) 128-152.

- [26] M. Calvo, R. García, S.R. Moinelo, Carbon foams from different coals, *Energy Fuels* 22 (2008) 3376-3383.
- [27] E. Rodriguez, R. García, Characterisation of boron-doped coal-derived carbon foams and their oxidation behaviour, *Fuel* 93 (2012) 288-297.
- [28] E. Rodriguez, I. Cameán, R. García, A.B. García, Graphitized boron-doped carbon foams: performance as anodes in lithium-ion batteries, *Electrochim. Acta* 56 (2011) 5090-5094.
- [29] J. Wang, J. Polleux, J. Lim, B. Dunn, Pseudocapacitive contributions to electrochemical energy storage in TiO₂ (Anatase) nanoparticles, *J. Phys. Chem. C* 111 (2007), 14925-14931.
- [30] A. Cuesta, P. Dhamelincourt, J. Laureyns, A. Martinez-Alonso, J.M.D. Tascon, Comparative performance of X-ray diffraction and Raman microprobe techniques for the study of carbon materials, *J. Mater. Chem.* 8 (1998) 2875-2879.
- [31] I. Cameán, A.B. Garcia, Graphite materials prepared by HTT of unburned carbon from coal combustion fly ashes: performance as anodes in lithium-ion batteries, *J. Power Sources*, 196 (2011) 4816-4820.
- [32] J. Biscoe, B.E. Warren, An X-Ray study of carbon black, *J. Appl. Phys.* 13 (1942) 364-371.
- [33] M.M. Dubinin, The potential theory of adsorption of gases and vapors for adsorbents with energetically nonuniform surfaces, *Chem Rev.* 60 (1960) 235-241.
- [34] A. Ramos, I. Camean, N. Cuesta, C. Antuña, A.B. Garcia, Expanded graphitic materials prepared from micro- and nanometric precursors as anodes for sodium-ion batteries, *Electrochim. Acta* 187 (2016) 496-507.

- 1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
- [35] K. Yamada, H. Ishikawa, C. Kamiwaki, M. Kawaguchi, The role of boron in B/C/N and B/C materials as anodes of sodium ion batteries, *Electrochemistry* 83 (2015) 452-458.
- [36] H. Lindström, S. Södergren, A. Solbrand, H. Rensmo, J. Hjelm, A. Hagfeldt, S.-E. Lindquist, Li⁺ ion insertion in TiO₂ (Anatase). 2. Voltammetry on nanoporous films, *J. Phys. Chem. B* 101 (1997) 7717-7722.
- [37] V. Augustyn, P. Simon, B. Dunn, Pseudocapacitive oxide materials for high-rate electrochemical energy storage, *Energy Environ. Sci.* 7 (2014) 1597-1614.
- [38] P. Liu, Y. Li, Y.-S. Hu, H. Li, L. Chen, X. Hyang, A waste biomass derived hard carbon as a high-performance anode material for sodium-ion batteries, *J. Mat. Chem. A* 4 (2016) 13046-13052.
- [39] N.A. Kumar, R.R. Gaddam, S.R. Varasani, D. Yang, S.K. Bhatia, X.S. Zhao, Sodium storage in reduced graphene oxide, *Electrochim. Acta* 214 (2016) 319-325.
- [40] E. Irisarri, A. Ponrouch, M.R. Palacin, Review-Hard carbon negative electrode materials for sodium-Ion batteries, *J. Electrochem. Soc.* 162 (2015) A2476-A2482.

TABLES

Table 1. Specific discharge (C_{disc}) and charge (C_{charge}) capacities in the 1st, 2nd and 50th cycles, irreversible capacity in the 1st discharge-charge cycle (C_{irr}) and capacity retention (R) parameters from the galvanostic cycling of graphitic carbon foams (GCFs) electrodes in 1M NaOTf in diglyme (NaOTf/DG) and in 1M NaOTf in tetraglyme (NaOTf/TTG), at an applied electrical current density of 37.2 mA g⁻¹.

Table 2. Boron content (B), structural (d_{002} , L_c , L_a) and textural parameters (S_{BET} , V_T , V_{MESO} , V_{MICRO}) of the graphitic carbon foams (GCFs).

Table 1

Specific discharge (C_{disc}) and charge (C_{charge}) capacities in the 1st, 2nd and 50th, cycles, irreversible capacity in the 1st discharge-charge cycle (C_{irr}) and capacity retention (R) parameters from the galvanostatic cycling of graphitic carbon foams (GCFs) electrodes in 1M NaOTf in diglyme (NaOTf/DG) and in 1M NaOTf in tetraglyme (NaOTf/TTG), at an applied electrical current density of 37.2 mA g⁻¹.

GCFs Electrode	$C_{\text{disc}}-C_{\text{charge}}/\text{mAh g}^{-1}$ (1 st cycle)		$C_{\text{disc}}-C_{\text{charge}}/\text{mAh g}^{-1}$ (2 nd cycle)		$C_{\text{disc}}-C_{\text{charge}}/\text{mAh g}^{-1}$ (50 th cycle)		$C_{\text{irr}}/\%$ (1 st cycle) ^a		$R_{\text{disc}}-R_{\text{charge}}/\%$ (2 nd - 50 th cycles) ^b	
	NaOTf/DG	NaOTf/TTG	NaOTf/DG	NaOTf/TTG	NaOTf/DG	NaOTf/TTG	NaOTf/DG	NaOTf/TTG	NaOTf/DG	NaOTf/TTG
0B24 [*]	202-107	268-126	128-108	155-130	103-104	126-118	47	53	80-97	81-91
0B26 [*]	164-89	146-69	102-89	86-66	89-87	71-65	46	53	87-98	82-98
0B28 [*]	124-79	46-24	98-80	31-25	77-75	24-22	36	48	79-94	77-88
5B24 ^{**}	238-93	204-86	132-94	108-86	102-88	84-79	61	58	78-94	78-92
5B28 ^{**}	146-102	137-78	113-101	95-78	102-99	81-76	30	43	90-98	85-97
10B24 ^{**}	274-110	221-93	129-109	108-92	95-90	90-91	60	58	74-83	84-99
MCF28 ^{***}	95-66	83-66	72-66	70-67	58-56	64-64	31	20	80-85	92-96

^a Irreversible capacity (%) = $[C_{\text{disc}} (1^{\text{st}} \text{ cycle}) - C_{\text{charge}} (1^{\text{st}} \text{ cycle})] [C_{\text{disc}} (1^{\text{st}} \text{ cycle})]^{-1} \times 100$

^b Capacity retention (%) = $[C_{\text{disc-charge}} (50^{\text{th}} \text{ cycle})] [C_{\text{disc-charge}} (2^{\text{nd}} \text{ cycle})]^{-1} \times 100$

* Non-doped graphitic carbon foams; ** Boron-doped graphitic carbon foams; *** Non-doped mesophase-based graphitic carbon foam

Table 2

Boron content (B), structural (d_{002} , L_c , L_a) and textural parameters (S_{BET} , V_T , V_{MESO} , V_{MICRO}) of the graphitic carbon foams (GCFs).

GCFs	B/wt. %	d_{002}/nm	L_c/nm	L_a/nm	$S_{\text{BET}}/\text{m}^2 \text{g}^{-1}$	$V_T/\text{cm}^3 \text{g}^{-1}$	$V_{\text{MESO}}/\text{cm}^3 \text{g}^{-1}$	$V_{\text{MICRO}}/\text{cm}^3 \text{g}^{-1}$
0B24	--	0.3379	26.6	54.4	50	0.11	0.09	0.02
0B26	--	0.3377	28.2	61.2				
0B28	--	0.3373	28.3	60.9	2.8	0.01	0.01	nd
5B24	2.20	0.3365	34.7	65.1	2.2	0.01	0.01	nd
5B28	0.20	0.3365	41.2	67.5	2.0	0.01	0.01	nd
10B24	3.40	0.3354	60.9	> 100	3.4	0.01	0.01	nd
MCF28	--	0.3366	59.5	> 100	< 1	nd	nd	nd

B, determined by ICP-MS; d_{002} , interlayer spacing; L_c , and L_a mean crystallite sizes along c and a axes; S_{BET} , surface area; V_T , total pore volume; V_{MESO} , mesopore volume; V_{MICRO} , micropore volume; $V_{\text{MESO}} = V_T - V_{\text{MICRO}}$; nd, no detected.

CAPTIONS FOR FIGURES

Figure 1. Discharge capacity vs cycle number plots from the galvanostatic cycling at 37.2 mA g⁻¹ of GCFs electrodes in NaOTf/DG and NaOTf/TTG electrolytes: (a) non-doped and (b) boron-doped.

Figure 2. Potential profiles of the galvanostatic cycling at 37.2 mA g⁻¹ of 0B28 and 5B28 electrodes in NaOTf/DG and NaOTf/TTG electrolytes (*left*) and the corresponding differential capacity plots (*right*).

Figure 3. 0B28 electrode in NaOTf/DG electrolyte: **(a)** Second cycle voltammograms at scan rates ν from 0.2 to 3 mVs⁻¹ and (b) b value (line slope) determination from the power law dependence of current i (A) on scan rate ν (mV s⁻¹) of the cathodic (sodiation) peaks 1 to 5.

Figure 4. Variation of b data with potential vs Na/Na⁺ for cathodic (sodiation) peaks (from CVs at the scan rate of 0.2 mV s⁻¹) of GCFs electrodes (a) non-doped and (b) boron-doped.

Figure 5. 0B28 electrode in NaOTf/DG: (a) scan rate ν dependence of the current i for the cathodic peaks (sodiation) 1, 2, 3, 4 and 5 (see Fig. 3) according to the equation $i/\nu^{1/2} = k_1 \nu^{1/2} + k_2$ [ref. 37] and calculated contributions of pseudocapacitive intercalation (CI) and diffusion-controlled intercalation (DCI) currents to the total measured current for each peak, and (b) calculated capacitive contribution to the total measured cathodic current in the CV at the scan rate of 0.2 mV s⁻¹.

Figure 6. Diffusion-controlled intercalation and pseudocapacitive intercalation contributions to the total sodiation (discharge) capacity of GFCs electrodes in 1M NaOTf/DG electrolyte.

Figure 7. Discharge capacity vs cycle number plots from the galvanostatic cycling at variable electrical current density (from 37.2 to 744.0 mA g⁻¹, and back to 37.2 mA g⁻¹) of GCFs electrodes: (a) non-doped and (b) boron-doped.

Figure 8. Discharge capacity vs cycle number plots from the prolonged galvanostatic cycling at 0.4 and 1.9 A g⁻¹ electrical current density of non-doped 0B24 and boron-doped 5B24 electrodes in NaOTf/DG electrolyte.

FIGURE 1

Figure 1. Discharge capacity vs cycle number plots from the galvanostatic cycling at 37.2 mA g⁻¹ of GCFs electrodes in NaOTf/DG and NaOTf/TTG electrolytes: (a) non-doped and (b) boron-doped.

FIGURE 2

Figure 2. Potential profiles of the galvanostatic cycling at 37.2 mA g^{-1} of 0B28 and 5B28 electrodes in NaOTf/DG and NaOTf/TTG electrolytes (*left*) and the corresponding differential capacity plots (*right*).

FIGURE 3

Figure 3. 0B28 electrode in NaOTf/DG electrolyte: **(a)** Second cycle voltammograms at scan rates ν from 0.2 to 3 mVs⁻¹ and **(b)** b value (line slope) determination from the power law dependence of current i (A) on scan rate ν (mV s⁻¹) of the cathodic (sodiation) peaks 1 to 5.

FIGURE 4

Figure 4. Variation of b data with potential vs Na/Na^+ for cathodic (sodiation) peaks (from CVs at the scan rate of 0.2 mV s^{-1}) of GCFs electrodes (a) non-doped and (b) boron-doped.

FIGURE 5

Figure 5. 0B28 electrode in NaOTf/DG: (a) scan rate v dependence of the current i for the cathodic peaks (sodiation) 1, 2, 3, 4 and 5 (see Fig. 3) according to the equation $i/v^{1/2} = k_1 v^{1/2} + k_2$ [ref. 37] and calculated contributions of pseudocapacitive intercalation (CI) and diffusion-controlled intercalation (DCI) currents to the total measured current for each peak, and (b) calculated capacitive contribution to the total measured cathodic current in the CV at the scan rate of 0.2 mV s^{-1} .

FIGURE 6

Figure 6. Diffusion-controlled intercalation and pseudocapacitive intercalation contributions to the total sodiation (discharge) capacity of GFCs electrodes in 1M NaOTf/DG electrolyte.

FIGURE 7

Figure 7. Discharge capacity vs cycle number plots from the galvanostatic cycling at variable electrical current density (from 37.2 to 744.0 mA g⁻¹, and back to 37.2 mA g⁻¹) of GCFs electrodes: (a) non-doped and (b) boron-doped.

FIGURE 8

Figure 8. Discharge capacity vs cycle number plots from the prolonged galvanostatic cycling at 0.4 and 1.9 A g⁻¹ electrical current density of non-doped 0B24 and boron-doped 5B24 electrodes in NaOTf/DG electrolyte.