#### **ORIGINAL PAPER**



# Development of vein graphite by optimizing the NaOH concentration in alkali roasting-acid leaching process for the anode application in rechargeable Li-ion batteries

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Received: 22 September 2022 / Revised: 3 November 2022 / Accepted: 5 November 2022 © The Author(s), under exclusive licence to Springer-Verlag GmbH Germany, part of Springer Nature 2022

#### Abstract

Vein graphite, notable for its high graphitization degree, purity, and crystallinity, has been investigated to be used as the anode material in rechargeable lithium-ion batteries (LIB), achieved with enhanced cycle life and capacity. However, the direct use of raw vein graphite as the anode material is not desirable because of its instability during battery cycling. In the present study, raw vein graphite was purified and modified using a combined alkali roasting and HCl acid leaching method in order to enhance its properties appropriate for the anode application in LIB. Various NaOH concentrations were tested for optimizing the purifying efficiency of vein graphite, which had already been treated with HCl acid leaching. Out of that, the 25 vol.% NaOH proves to be the optimum concentration for alkali roasting. The following material characterization reveals that the tested method is capable of upgrading the carbon content of raw vein graphite up to 99.9% by effectively removing impurities while enhancing the properties appropriate for the battery application. Electrochemical characterization shows an improved cycle stability and capacity retention with 99.9% Coulombic efficiency in the developed material. Altogether, this novel combined alkali roasting and HCl acid leaching method have resulted in adequate purification and modification as well as promising electrochemical performance for vein graphite for the anode application in rechargeable Li-ion batteries.

Keywords Vein graphite · LIB · Acid leaching · Alkali roasting · Electrochemical performance

## Introduction

The global market for rechargeable lithium-ion batteries (LIB) has grown rapidly due to the booming demand for uninterruptible power supplies, smart devices, and plug-in vehicles. To meet these highly challenging demands, the capacity, cycling life, and rate capability of the LIB needed to be improved. Hence, the electrode materials become an important factor in improving the performance of LIB. The high capacity, long cycling life, low cost, and unfailing

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safety ought to be the most important characteristics of an electrode material. In particular, the materials presently used for electrodes in LIB are needed to be further developed to enhance power and energy density, while maintaining excellent cycling stability. As a result, researchers have concentrated their efforts primarily on the development of anode and cathode materials of LIB [1–28]. For anodes, the presently preferred material is graphite, though Si and Sn metals too are becoming promising candidates for future anodes [1].

Graphite possesses a high graphitization degree, high purity, and high crystallinity. It has been developed for the use as the anode of LIB to achieve a long cycling life with a satisfactory capacity [2]. Graphite is mainly categorized into natural graphite and synthetic graphite. Further, natural graphite can be classified into flake graphite, vein graphite, and amorphous graphite according to the degree of crystallinity. Though flake graphite is mainly used for the anode of LIB, it has a lower retention capacity than the theoretical capacity of graphite (372 mA h g<sup>-1</sup>) [3–5]. Further, flake graphite has to be processed through a costly spheroidization

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process into spherical graphite (SpG), which is made up of well-rounded spherules that are stacked to provide a long cycling life, high capacity and excellent rate capability for LIB [4].

Vein graphite (VG) is significant for its high crystallinity, high purity, limited occurrences, extensive mineralization that typically exists with around 95–99% of carbon content [6]. Importantly, VG particles themselves possess a similar morphology to SpG, hence no actual necessity for spheroidization prior to the battery application. However, some impurities or gangue minerals present in VG are one of the major hindrances for their direct use in LIB. The amount of gangue minerals contained in graphite depends on the mode of occurrence and nature of graphite veins [6, 7, 29]. Nevertheless, the removal of those impurities is essential for VG to achieve a carbon content of around 99.9% with minimal metallic impurities for its successful use as the anode material in LIB.

The most common graphite purification processes developed so far are flotation, acid leaching, and alkali roasting methods. Naturally, hydrophobic graphite is concentrated primarily by flotation, but this technique is incompetent to purify over 98% of carbon content [8]. Therefore, chemical purification processes are required to purify graphite in order to obtain high-purity graphite with sufficient capacity to be used as the anode material in LIB. Out of the main chemical purification techniques, the acid leaching method uses a variety of acids such as HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub>, and HF to remove impurities, effectively [8, 30]. On the other hand, the alkali roasting methods, which use bases combined with thermal treatment, can also be employed to remove impurities in graphite [30, 31]. These chemical purification methods are capable of enhancing the carbon content of graphite above 98% [8, 30, 31]. However, none of these purification methods alone is capable of achieving the higher purity requirement of graphite needed for the anode material in LIB. Therefore, purifying graphite to enhance its carbon content to 99.9% needs further research on process development and optimization.

Hence, in the present study, the HCl-based acid leaching method and the NaOH based alkali roasting method are combined to increase the purity of raw graphite coupled with enhanced capacity together with long cycling life when used for the anode application in LIB. For that, the optimized concentration of HCl acid in the acid leaching method and the optimized concentration of NaOH base in the alkali roasting method should be determined. The optimum concentration of HCl acid for graphite has already been found to be as 5 vol. % by our previous study and reported elsewhere [6, 7, 32]. The present study combines that finding on HCl acid leaching together with the optimum NaOH concentration of the alkali roasting method, which will be determined at the initial part of this study. Thereafter, the gained knowledge is utilized to optimize the NaOH concentration in the novel combined alkali roasting-acid leaching process developed in the present study for preparing vein graphite for the anode application in rechargeable Li-ion batteries.

# **Materials and methods**

#### **Chemical treatment**

Though several different structural varieties of VG have been reported [29, 33], the Needle-Platy graphite (NPG) variety was used for this study by considering its high purity and high crystallinity [29]. Graphite lumps were broken into small chips and the chips were grounded using a vibratory disk mill. The milled graphite powder was sieved by using a mechanical sieving setup. The present study was carried out using a graphite powder of size  $< 53 \mu m$  and analytical reagent grade chemicals. Powdered raw graphite (3.0 g) was treated with NaOH concentrations of 20.0, 25.0, 30.0, 35.0, and 40.0 vol. %, separately and roasted under air (550 °C) for 1 h. The roasted mixtures were washed with deionized water until neutral and then subjected to vacuum filtering followed by vacuum drying. The residues were acid leached with 10.0 vol. % H<sub>2</sub>SO<sub>4</sub> solution and stirred for 1 h at room temperature. After leaching, the precipitates were washed until neutral using de-ionized water and the neutralized residue was dried in a vacuum oven. Based on the outcome of this alkali roasting study, the optimum NaOH concentration for the alkali roasting process was selected. Then for the combined process, the alkali roasting was performed using the selected optimum NaOH concentration with 3.75 g of graphite powder, which had already been subjected for the acid leaching with 5 vol. % HCl[32].

#### Material characterization

Carbon content analysis of the raw and treated graphite samples was carried out by using the ASTM-561C method [7, 9]. X-ray diffractograms of powdered graphite samples were obtained using Rigaku Ultima IV X-Ray Diffractometer (XRD) under Cu K<sub> $\alpha$ </sub> radiation ( $\lambda = 1.5406$  Å). The measurement was taken at the step resolution of 0.02° and the time step of 2 s. The KBr pellet method was used to obtain the Fourier transform infrared (FTIR) spectrum using a Thermo Scientific Nicolet is50 FTIR spectrometer. The morphological analysis of the graphite samples was carried out by using the scanning electron microscopy (SEM) (EEVO/LS ZEISS). Renishaw InVia Raman spectroscopic analysis.

#### **Electrochemical characterization**

Graphite powder, acetylene black, and polyvinylidene fluoride dispersed in N-Methyl-2-pyrrolidone were used to prepare the slurry for tape casting the graphite electrodes. The slurry was cast on a Cu foil by employing the doctor blade method, and the graphite electrodes were cut using an electrode cutter. The active material loading of the graphite electrodes used for the battery assembling was  $3.458 \text{ mg cm}^{-2}$ . CR 2032 coin-cells with a graphite anode/LiPF<sub>6</sub>/Li cell configuration were assembled in an argon gas filled glovebox (LC Technology Solutions Inc.), with Li as the counter electrode and lithium hexafluorophosphate solution in ethylene carbonate and dimethyl carbonate (1.0-M LiPF<sub>6</sub> in EC/DMC = 50/50 (v/v), battery grade) as the electrolyte. A battery tester (Landt CT2001A) was used to perform the Galvanostatic charge-discharge test of the assembled coin cells in the range 0.002-1.5 V at the rate of 0.1 C. Cyclic voltammetry (CV) analysis was obtained by using the electrochemical workstation (Biologic Science Instruments SAS - VMP3) at 0.002-1.5 V with a scan rate of 0.02 mV s<sup>-1</sup>. The same electrochemical workstation was used for the electrochemical impedance spectroscopy (EIS) measurements in the frequency range from 200 to 100 kHz, at the signal amplitude of 10 mV.

## Results

## Effect of varying NaOH concentration of the alkali roasting (AR) method

Powdered raw vein graphite (RVG) was treated with different concentrations of NaOH in the range of 20–40 vol. %. The carbon content and impurity removal efficiency of raw and treated graphite are presented in Table 1. Here the RVG-AR-20, RVG-AR-25, RVG-AR-30, RVG-AR-35, and RVG-AR-40 are graphite samples after subjecting to alkali roasting with 20, 25, 30, 35, and 40 NaOH (vol. %), respectively.

 Table 1 Carbon content and impurity removal efficiency of raw graphite and alkali roasted graphite treated with different concentrations of NaOH

Sample name	NaOH (vol %)	Carbon con- tent (%)	Impurity removal effi- ciency (%)
RVG	_	97.5	-
RVG-AR-20	20.0	98.8	52.0
RVG-AR-25	25.0	99.2	68.0
RVG-AR-30	30.0	99.1	64.0
RVG-AR-35	35.0	99.1	64.0
RVG-AR-40	40.0	98.7	47.0

The carbon content of RVG was 97.5%, and the resultant carbon content of alkali roasted samples were 98.8%, 99.2%, 99.1%, 99.1%, and 98.7% for RVG-AR-20, RVG-AR-25, RVG-AR-30, RVG-AR-35, and RVG-AR-40, respectively. Based on Table 1, RVG-AR-30 and RVG-AR-35 samples had the same impurity removal efficiency of 64.0% while RVG-AR-40 sample showed the lowest impurity removal efficiency. On the other side, when compared with RVG-AR-25, RVG-AR-20 showed lower purity with lower impurity removal efficiency. Accordingly, the RVG-AR-25 shows the highest percentage of carbon content (99.2%) with the highest impurity removal efficiency (68.0%).

Figure 1 shows the X-ray diffractograms obtained for raw and alkali roasted graphite. The diffraction peaks of RVG with 20 values of 26.5°, 42.3°, 44.5°, 52.8°, 54.6°, and 59.8° corresponded to the d-spacing values and crystal planes of characteristic peaks 3.35 Å (002), 2.13 Å (100), 2.03 Å (101), 1.73 Å (102), 1.68 Å (004), and 1.55 Å (103), respectively. They could be indexed to the hexagonal structure of graphite of the space group P6<sub>3</sub>/mmc (194) [JCDPS Card no: 75–1621] with cell parameters of a=b=2.463 Å and c = 6.714 Å. Further, as seen in Fig. 1, all these alkali roasted graphite materials could retained this relevant graphite phase. Apart from those diffraction peaks corresponding to the relevant graphite phase, some extra peaks of lesser intensities can be identified from the diffractogram of RVG. This is an indication to the existence of impurities that are incorporated into the crystalline lattice as well as the gangues occur as mineral inclusions in raw vein graphite [7, 34, 35]. Some of these impurities could be identified as pyrite [JCPDS Card no: 21-0432], quartz [JCDPS Card no: 33-1161], chalcopyrite [JCDPS Card no: 85-1575]/calcite [JCDPS Card no: 86–2340], and siderite [JCPDS Card no: 29-0696]. Compared to that of RVG, those peaks related to the impurity phases are partially lessened or completely absent in alkali roasted samples (Fig. 1). Importantly, the corresponding diffractogram of RVG-AR-25 indicates for very successful elimination of the pyrite, quartz, and siderite impurity phases with a partial removal of other impurities of chalcopyrite /calcite. However, when compared with RVG-AR-25, the impurity removal is not as effective in the RVG-AR-20. As seen in Fig. 1, while the traces for quartz phase is still evident in RVG-AR-20, the RVG-AR-25 have successfully removed the quartz phase, and that may be due to the presence of hydroxyl ions in the solution attacked at a specific concentration as reported elsewhere [36, 37]. Hence, altogether this study reveals that 25 vol. % is the most effective NaOH concentration for purifying RVG by the present alkali roasting method.

Figure 2a shows the FTIR spectra obtained for raw graphite and alkali roasted graphite in the absorbance mode in the range from 4000 to 500 cm<sup>-1</sup>. FTIR analysis helps to identify the presence of oxygen and other functional groups

**Fig. 1** X-ray diffractograms of raw graphite and alkali roasted graphite treated with different concentrations of NaOH



attached to the surface and hence to determine the capability of this alkali roasting method for modifying the surface. In the spectrum of RVG (Fig. 2a), there are no significant peaks relevant to any functional groups, but a weak band appears around 2350 cm<sup>-1</sup> due to the adsorbed water molecule, as reported elsewhere [38]. According to Fig. 2a, there are noticeable differences in the spectra of alkali roasted graphite with a number of distinct peaks appeared in the spectrum. The peaks related to stretching vibration O-H (alcohol group) and the bending O-H (alcohol group), which appear at 3450 cm<sup>-1</sup> and 1400 cm<sup>-1</sup>, respectively, occur when the hydroxyl is generated by the adsorption of the trace amount of moisture [10, 38, 39]. Due to the O-H band overlapping with in-plane vibrations of the C = C band of the hexagonal aromatic ring from the graphite, the conjugated C = Cbond is visible at 1650  $\text{cm}^{-1}$  [10, 38, 39]. The spectra of RVG-AR-35 (Fig. 2a) and RVG-AR-40 (Fig. 2a) show a peak around 1080 cm<sup>-1</sup>, which is a characteristic peak for C-O (secondary alcohol group - alkoxy) indicating that original extended conjugated  $\pi$  orbital system of the natural graphite had been destroyed and C-O group has been inserted into graphite structure [38]. Furthermore, the spectrum of RVG-AR-40 shows a peak around 1520 cm<sup>-1</sup> due to C=O (carbonyl group), which is likewise responsible for destroying the conjugated  $\pi$  orbital system of the natural graphite [38]. Though comparable patterns can be seen in the spectra of RVG-AR-20, RVG-AR-25, and RVG-AR-30, the spectrum of RVG-AR-25 does not exhibit evidence for the C-O group beginning to emerge at 1080 cm<sup>-1</sup>. Altogether, compared to the spectrum of RVG, the FTIR spectra of the alkali roasted samples have additional functional groups that could be formed on the graphite surface during the alkali roasting process. According to Piazza et al. (2019), these additional functional groups are created due to hydrogenated double bonds and the number of saturated sp<sup>3</sup> carbon atoms in the samples [40]. Therefore, FTIR spectrum analysis reveals that while successfully purifying graphite, the alkali roasting process can also modify the graphite surface.

Figure 2b shows the Raman spectra for raw graphite and alkali roasted graphite. The Raman spectroscopy can be used to identify the defects of structural morphology, layer stacks, crystallinity, and molecular interactions of graphite [41, 42]. According to Fig. 2b, the most prominent features of the Raman spectrum of RVG are D band, G band, D+D'band, and 2D band appearing around  $1350 \text{ cm}^{-1}$ ,  $1582 \text{ cm}^{-1}$ , 2443 cm<sup>-1</sup>, and 2700 cm<sup>-1</sup>, respectively. The G band occurs due to the bond stretching of all pairs of sp<sup>2</sup> carbon networks, and the D band appears as a disorder-induced band due to the breathing modes of  $sp^2$  carbon networks [42, 43]. According to Fig. 2b, the Raman spectra of all the alkali roasted graphite show the existence of the G band, D band, D+D' band, and 2D band, which are prominent features in the Raman spectrum of graphite. Moreover, G band, 2D band, and D+D' band are present with approximately the



Fig.2 a FTIR spectra obtained for raw graphite and alkali roasted graphite treated with different concentrations of NaOH. b RAMAN spectra obtained for raw graphite and alkali roasted graphite treated

with different concentrations of NaOH. c SEM image obtained for raw graphite. d SEM image obtained for 25 vol. % NaOH treated alkali roasted sample

same intensity in all these spectra. However, compared to RVG, the alkali roasted samples exhibit low D band intensity (Fig. 2b). According to Piazza et al. (2019), narrow D and D + D' peaks have low relative intensities caused by defects such as vacancies, edge defects, or C-H binding [40]. Moreover, the intensity of the D band decreases as the edge behaves like a structural defect necessary for momentum conservation in the double resonance Raman process

[42]. Hence, as reported in previous studies, the D band and D + D' band in the Raman spectrum of RVG are activated by edge defects [42, 43]. Furthermore, according to Fig. 2b, the intensity of the D band of the RVG-AR-25 appeared to be the lowest among these alkali roasted samples. The integrated intensity ratio  $I_D/I_G$  for the D band and G band can be used to characterize the defect quantity in graphite [42]. As given in Fig. 2b, the  $I_D/I_G$  of RVG is 0.24, while it is for

RVG-AR-20, RVG-AR-25, RVG-AR-30, RVG-AR-35, and RVG-AR-40 are 0.09, 0.03, 0.05, 0.04, and 0.07, respectively. As same with having the lowest D band intensity, the RVG-AR-25 possesses also the lowest integrated intensity ratio. Altogether this Raman analysis indicates for having the fewest edge defects in RVG-AR-25 graphite with compared to the other alkali roasted graphite samples. Figure 2c and Fig. 2d show the SEM images obtained for raw and alkali roasted RVG-AR-25 graphite samples. The SEM image of RVG (Fig. 2c) shows a rough and platy appearance of the edges of graphite particles. However, as seen in Fig. 2d, this rough appearance of the edges has been decreased indicating that the alkali roasting had caused to smoothen the edges.

As already presented above of the present study, high purity of over 99% carbon content could be achieved by the alkali roasting techniques while RVG-AR-25 showing the highest outcome of 99.2%. Further, the XRD phase analysis revealed that alkali roasting could successfully remove impurities such as pyrite, siderite, chalcopyrite/calcite, and quartz while preserving the crystal structure of graphite with the space group P6<sub>3</sub> / mmc. Specially, the RVG-AR-25 is showing the best performance in purification by successfully eliminating pyrite, quartz, and siderite also with partial removal of chalcopyrite/calcite phases. In addition, according to the FTIR analysis, additional functional groups are formed during the alkali roasting process on the graphite surface. This formed carboxyl and alkoxy group could destroy the graphite structure and saturates the sp<sup>3</sup> carbon atoms leading to ultimate decrease of capacity retaining. As RVG-AR-20, RVG-AR-25, and RVG-AR-30 show less additional functional groups than alkali roasted graphite, they can be more suitable for the intended battery anode application. Finally, Raman analysis reveals that the RVG-AR-25 has the fewer edge defects hence the best among the studied alkali roasted graphite samples while the SEM study also supporting it with the existence of smooth edges. Altogether, based on all these findings, 25 vol. % is selected as the optimum NaOH concentration for alkali roasting of vein graphite.

#### Purification of graphite by acid leaching method

Our previous study has shown that the HCl acid leaching method can be optimized for purifying vein graphite. In that study, which was performed with adding 3.75 g of raw vein graphite powder, the optimum HCl concentration for acid leaching was determined to be 5 vol. %, as presented elsewhere [6, 7, 32]. According to Amaraweera et al. (2013), the carbon content could be enhanced from 99.86% of raw vein graphite to 99.97% by the HCl acid leaching method [6, 7, 32]. Likewise, the HCl acid leaching process, performed under the present study to prepare the acid leached vein graphite (RVG-AL), could increase the carbon content from

97.5% of raw vein graphite (RVG) up to 99.2% of RVG-AL, by resulting 68.0% of impurity removal percentage.

Figure 3 shows the X-ray diffractograms, FTIR spectra, Raman spectra, and SEM images obtained for RVG and RVG-AL samples. By comparing those two XRD diffractograms of RVG and RVG-AL (Fig. 3a), it shows the successfulness of this HCl acid leach method to remove the pyrite and siderite impurity phase. These impurities may react with HCl and release Fe, Mg, Ca, and Cu into the solution [6]. However, HCl is ineffective in removing silicate minerals such as quartz, as well as sulfate and carbonate impurities that are physically attached to and intercalated with graphite [6]. Hence, it may be the reason for the reported lesser impurity removal efficiency in the current study with acid-leached graphite, which possesses a higher quartz percentage. Furthermore, the XRD analysis confirms the preserving of the high crystallinity and the required graphite crystal structure of the space group  $P6_3$  / mmc by the employed HCl acid leaching process, also reported in other recent findings [6, 8, 30, 32, 44].

Based on SEM images (Fig. 3b and Fig. 3c), RVG-AL particles shows of having smooth edges. A similar behavior has been reported by Amaraweera et al. (2014) where the basal and edge plane surfaces of raw vein graphite showing a lesser surface roughness and appearing to be "cleaned" after the HCl acid leaching process [11]. According to the Raman spectra (Fig. 3e) of RVG and RVG-AL, the intensities of the D band, 2D band, and D + D' band are around 1350 cm<sup>-1</sup>,  $2700 \text{ cm}^{-1}$  and  $2443 \text{ cm}^{-1}$ , respectively. In addition, these spectra show another major peak existing around 1582 cm<sup>-1</sup> termed as G band. The  $I_D/I_G$  of the RVG-AL sample is 0.076; however, as reported above, this ratio is 0.24 for RVG. When considering the relationship of this  $I_D/I_G$  ratio with the degree of edge defect as explained previously, it indicated that RVG-AL possesses fewer edge defects than those of RVG. Further, according to the FTIR spectra (Fig. 3d), in comparison that of RVG, there isn't any evidence for forming additional functional groups in RVG-AL by the HCl acid leaching process. It indicates that while being as an effective purification method, the HCl acid leaching process does not cause any modification to the surface of the graphite.

# Effect of combining acid leaching method and alkali roasting method on the efficiency of graphite purification

Table 2 presents the carbon content and impurity removal efficiency for raw graphite (RVG), alkali roasted raw graphite by 25 vol. % of NaOH (RVG-AR-25), acid leached graphite by 5 vol. % of HCl (RVG-AL), and finally the acid leached (with 5 vol. % of HCl) graphite treated with alkali roasting at 25 vol. % of NaOH (AL-AR-25). The 25 vol. % of optimum NaOH concentration for the alkali roasting



**Fig.3 a** X-Ray diffractograms obtained for RVG and HCl acid leached graphite. **b** SEM image obtained for RVG. **c** SEM image obtained for HCl acid leached graphite. **d** FTIR spectra obtained for

 Table 2
 Carbon content and impurity removal efficiency for RVG,

 RVG-AR-25, RVG-AL, and AL-AR-25 samples

Sample name	RVG	RVG-AR-25	RVG-AL	AL-AR-25
Carbon content %	97.5	99.2	99.2	99.9
Impurity removal efficiency %	-	68.0	68.0	96.0

RVG and HCl acid leached graphite. e RAMAN spectra obtained for RVG and HCl acid leached graphite

process, determined under the initial part of the study, was used for the alkali roasting of already acid leached (with 5 vol. % HCl) graphite, by the combined process introduced in the present study. According to Table 2, RVG-AR-25 and RVG-AL show the same carbon content of 99.2% and impurity removal efficiency. However, very importantly, the combined method introduced by the present study, reveals its greater effectiveness on purification by resulting in a very high purity of 99.9% with 96.0% of impurity removal efficiency. Moreover, Fig. 4 shows the X-ray diffractograms, FTIR spectra, Raman spectra, and SEM images obtained for these RVG, RVG-AR-25, RVG-AL, and AL-AR-25 samples. According to the XRD diffractograms (Fig. 4a), the RVG contains the impurities phases mainly of pyrite (Py), quartz (Qz), siderite (Sid), and chalcopyrite/calcite (Cha/Ca), while RVG-AL shows only quartz and chalcopyrite/calcite. It suggests that quartz and chalcopyrite/calcite may be intercalated with

graphite inclusions that cannot be completely detached from graphite by acid leaching [6]. In the diffractogram of AL-AR-25 graphite, though the peaks of the major crystallographic graphite phase are much prominent, it still evidences for a very minor peak indicating the existence of a minor phase of chalcopyrite/calcite. Only this minor peak of chalcopyrite/ calcite impurity can be visible and identified in AL-AR-25 because the other minor impurity phases have already been



Fig. 4 a X-ray diffractograms for RVG, RVG-AR-25, RVG-AL, and AL-AR-25 graphite samples. b SEM image obtained for AL-AR-25. c FTIR spectra obtained for RVG, RVG-AL, RVG-AR-25, and AL-AR-25. d RAMAN spectra obtained for RVG, RVG-AL, RVG-AR-25, and AL-AR-25.

eliminated. Furthermore, the interplanar distance (d-spacing) of AL-AR-25 was calculated to be 3.36 Å, and it shows a 0.01 Å decrement in the d-spacing with compared to RVG. It gives a strong indication for the elimination of impurities that had occupied the interlayer space, as reported elsewhere [8]. These findings again reveal the effectiveness of this novel combined purification process. Further, the phase analysis confirms that the AL-AR-25 signifies the lattice structure that is contained in the space group P6<sub>3</sub> / mmc (194). Therefore, while successfully purifying graphite this combined process also preserves the crystal structure of graphite, which is preferred for the anode application of the LIB.

Figure 4d displays Raman spectra obtained for raw graphite and alkali roasted graphite. The Raman spectra reveal the existence of the prominent peaks such as G band, 2D band, D+D' band, and D band even after subjecting graphite to this combined purification process. D band intensity of RVG is highest, revealing that it has a high level of edge defects [42, 45]. Similarly, RVG-AL indicates for the highest level of edge defects when compared its D band intensity with other purified graphite. Furthermore, interestingly the D band intensity of AL-AR-25 is lowest with the lowest  $I_D$ /  $I_{G}$  is 0.03, as discussed earlier this indicates for few edge defects with less disorder in this AL-AR-25. On the other hand, RVG-AR-25 and AL-AR-25 show similar D band intensity with very close  $I_D/I_G$  values of 0.031 and 0.030, respectively, with a distinction of 0.001. Importantly, as discussed earlier both these materials indicate for having few edge defects with less disorder. As both these materials have been developed through subjecting to NaOH alkali roasting process, it might be due to the improvements instigated by this employed alkali roasting method. According to Fig. 4b, the SEM image of AL-AR-25 has smoother edges than the RVG-AR-25 (see Fig. 2d) and the RVG-AL (see Fig. 3d). Furthermore, the AL-AR-25 has small gaps between the extremely thin plates. Hence, AL-AR-25 has smoothened edges with the gaps than the RVG-AR-25 and RVG-AL.

Figure 4c shows the FTIR spectra obtained for raw graphite and alkali roasted graphite. There are no evidences for the existence of any additional functional groups in both RVG and RVG-AL. However, RVG-AR-25 and AL-AR-25 show the existence of some additional peaks in their respective spectra. Compared to the RVG-AR-25, the AL-AR-25 has the characteristic peak for C-O (secondary alcohol group – alkoxy). On the other hand, neither of the spectra exhibits any additional groups except for stretching vibration O-H (alcohol group), bending O-H (alcohol group), and conjugated C = C bond. However, in the AL-AR-25, the conjugated  $\pi$  – orbital system of the natural graphite was destroyed, and the C-O group was inserted into the graphite structure [38]. Hence, it reveals that the surface of the AL-AR-25 graphite had been modified by this combined purification introduced by the present study.

The carbon content measurement resulted in a very high purity of 99.9% for this AL-AR-25 developed through the combined purification process introduced in the present study. Further, the XRD phase analysis confirmed the presence of high crystallinity with significantly eliminated impurity phases while preserving the required graphite phase. Moreover, the Raman analysis revealed of having fewer edge defects while SEM evidenced for smoother edges for this AL-AR-25 graphite particles. Finally, the FTIR analysis indicated for considerable modification to the graphite surface and that will be an added advantage for the intended application. Based on the outcome, this AL-AR-25 can be proposed as a potential candidate to be further investigated for the intended anode application of in LIB.

## Electrochemical characterization for raw graphite and developed graphite

The important and crucial part of the present work is the Galvanostatic charge/discharge characterization of the developed materials. Each charge-discharge cycle consists of a 0.1 C rate charging process and 0.1 C rate discharging process, under the constant current/ constant voltage mode. Based on cycling performance shown in Fig. 5, RVG exhibited the initial specific discharge capacity  $(DCC_{sp})$  of 447.4 mA h  $g^{-1}$ . In spite of that, its first cycle specific charge capacity (CC<sub>sp</sub>) was 259.5 mA h  $g^{-1}$  with a 58.0% Coulombic efficiency. During the first cycle of RVG, a larger initial DCC<sub>sp</sub> has been observed with a lower Coulombic efficiency. As reported in the previous studies, electrolyte reduction occurs on the graphite surface during the first lithiation of the graphite anode, forming a solid electrolyte interphase (SEI), which is ionically conductive but electronically insulating [1, 12–14]. This anode SEI typically consists of reduction products of electrolytes generated through the reactions between electrode and electrolyte due to the electron leakage from the anode [14]. Due to anode SEI formation, the first cycle shows a low Coulombic efficiency and a large specific discharge capacity resulting in an irreversible capacity loss due to the decomposition of electrolytes and subsequent use of  $Li^+$  as a charge carrier [15]. The irreversible capacity loss means the capacity difference between the charge and discharge curves [12, 16]. As determined from Fig. 5, the irreversible capacity loss for the RVG is 187.0 mA h  $g^{-1}$ .

The second cycle DCC<sub>sp</sub> of RVG is 282.6 mA h g<sup>-1</sup> with an irreversible capacity loss of 17.2 mA h g<sup>-1</sup> and Coulombic efficiency of 93.9% (Fig. 5). During the second cycle, DCC<sub>sp</sub> and irreversible capacity loss have been decreased while increasing the Coulombic efficiency, indicating the formation of a stable SEI mainly during the first intercalation of RVG. The SEI acts as a protective layer, preventing continuous electrolyte decomposition and solvent co-intercalation into graphitic layers during

Fig. 5 a Cycling performance obtained for RVG, RVG-AL, RVG-AR-25, and AL-AR-25. b Coulombic efficiency obtained for RVG, RVG-AL, RVG-AR-25, and AL-AR-25 with insert of Nyquist plots of after first lithiation obtained for RVG-AL and AL-AR-25



subsequent cycles [1, 17]. As seen in Fig. 5, during the 4th to 35th cycles, the RVG shows slightly varied  $DCC_{sp}$  due to the continuous growth of the SEI film at the electrode/ electrolyte interface at the anode, until stabilization of the Coulombic efficiency. Thereafter, RVG becomes stable after the 35th cycle and remains over 50 cycles or more

by maintaining the Coulombic efficiency of over 99.0%. At that time,  $DCC_{sp}$  is around 200 mA h g<sup>-1</sup>, and the specific discharge capacity of raw vein graphite remains close to 200 mA h g<sup>-1</sup>, even after 50 cycles.

Specific discharge capacity and corresponding Coulombic efficiency of the first cycle of AL-AR-25, RVG-AL, and RVG-AR-25 are 377.6 mA h  $g^{-1}$  (83.0%), 375.8 mA h  $g^{-1}$ (84.1%), and 323.3 mA h g<sup>-1</sup> (86.9%), respectively (Fig. 5). AL-AR-25 exhibits lowest Coulombic efficiency and the highest discharge capacity in the first cycle among them. In subsequent cycles, these developed graphite materials could maintain their DCC<sub>sp</sub> 300 mA h g<sup>-1</sup> and Coulombic efficiency of over 99.0%, even after 50 cycles. However, as seen in Fig. 5, the specific discharge capacity of the AL-AR-25 appeared to be stabilized only after the 5th cycle, then resulting in a very high Coulombic efficiency of 99.9%. Some previous studies have indicated for similar situations where the decomposition of the electrolyte in the phase between the treated graphite and the electrolyte, that is, needed to build up the SEI film by passivating the electrodes, is much milder than for raw graphite [18]. Hence, such performance can be related to having more stable active sites and space for the storage of Li<sup>+</sup> and maintaining the capacity due to the highest Li<sup>+</sup> storage capacity [14, 19]. Accordingly, AL-AR-25 should possess the highest capacity retention when compared to the other developed graphite in the present study.

The Nyquist plots obtained for after first lithiation of RVG-AL and AL-AR-25 are shown in the insert of Fig. 5b. Both these Nyquist plots show an overall nature consisting of a semicircle with a spike. In general, this EIS study showed a considerable decreasing in the diameter of the semi-circle, hence a significant lowering of the impedance, after first lithiation. This could be related to the consequences arising with formation of the SEI layer mainly during the first lithiation, where the formation of the SEI layer facilitates Li<sup>+</sup> ion diffusion, potentially increasing the cell's ionic conductivity [9, 20-22]. Conversely, all these treated graphite exhibit somewhat similar impedance behavior following first lithiation, consistent with discharge specific capacity and Coulombic efficiency. According to the EIS plots present in the insert of Fig. 5b, the impedance of the acid leached RVG-AL is higher than that of AL-AR-25, which was prepared by alkali roasting of the same already acid leached RVG-AL. This lower impedance in the AL-AR-25 could definitely be related to the enhanced ionic conductivity, hence Li<sup>+</sup> ion diffusion, in the cell. That indicates for the positive influence instigated by introducing a second purification step using alkali roasting to the already acid leached graphite, under this novel combined purification process introduced in the present study.

Figure 6a shows the Galvanostatic charge/discharge cycling profiles obtained for RVG, RVG-AL, RVG-AR-25, and AL-AR-25. All of the discharge curves show a characteristic drop in the potential from the open circuit voltage (OCV) to around 0.2 V vs Li/Li<sup>+</sup> (b of Fig. 6a). In addition, a small plateau is observed at 0.6 V vs Li/Li<sup>+</sup> (a of Fig. 6a). This plateau can be attributed to the intercalation of solid-solution-type lithium thorough graphite particles and the decomposition of electrolyte to accumulate the SEI

layer on the surface of the graphite [15]. The plateaus (b, c, d in Fig. 6a) observed in the potential ranges from 0.2 V vs Li/Li<sup>+</sup> to 0 V vs Li/Li<sup>+</sup> correspond to the phase transition of lithium intercalation/deintercalation in graphite, as also reported in the previous studies [15, 19]. These voltage profiles clearly show the appearance of phase transitions. Furthermore, these phase transitions can be electrochemically monitored when performing a cyclic voltammogram. In the lithiation-delithiation process, the phase transitions start from LiC<sub>72</sub> and undergoes through LiC<sub>36</sub>, LiC<sub>27</sub>, LiC<sub>18</sub>, LiC<sub>12</sub>, up to LiC<sub>6</sub> [9, 15, 19].

Figure 6b and Fig. 6c illustrate the comparison of the 1st, 2nd and 50th charge/discharge cycles of RVG and AL-AR-25, respectively. Compared to RVG (Fig. 6b), the plateau of AR-AL-25 (Fig. 6c) increases sharply when the capacity approaches approximately 300 mA h  $g^{-1}$ , and the lower plateau shows a sacrificial capacity of ~ 100 mA h  $g^{-1}$ . According to Ma et al. (2018), the cycling profiles explain the various Li<sup>+</sup> storage mechanisms in the graphite and the perfect reversibility of the lithiation/delithiation process [19]. Therefore, the cycling profiles of raw graphite and the treated graphite display the Li<sup>+</sup> storage capacity and the perfectness of the reversibility lithiation/delithiation process. Among them, as seen in Fig. 6c, the AL-AR-25 possesses the largest Li<sup>+</sup> storage capacity with a perfect reversibility in the lithiation and delithiation process.

Figure 7 shows the cyclic voltammograms obtained for the first cycle of RVG and AL-AR-25 graphite electrodes. In the cyclic voltammogram of RVG, there is a large irreversible peak exist near 0.2 V vs Li/Li<sup>+</sup> (b in Fig. 7), which can be attributed to the delayed infiltration of the electrolyte into the inside of the anode and the start to the formation of SEI, as reported elsewhere [9, 18, 19]. In addition, another peak is observed near 0.02 V vs Li/Li<sup>+</sup> (f in Fig. 7) that is related to the lithium ion intercalation and formation of LiC<sub>6</sub> at the graphite anode [9, 18, 19]. However, compared to the RVG, the cyclic voltammogram of AL-AR-25 shows the existence of some different plateaus. The large irreversible peak near 0.5 V vs Li/Li<sup>+</sup> (a in Fig. 7) can be attributed to electrolyte decomposition and graphite exfoliation, as also reported in previous studies [9, 18, 19]. In addition, there are three other small peaks that can be observed at a potential lower than 0.2 V vs Li/Li<sup>+</sup>. These peaks can be attributed for the lithium intercalation and phase transitions [9, 18, 19]. During the anodic sweep, the two other small peaks in RVG and three other small peaks in AL-AR-25 can be observed. These peaks could be formed by the deintercalation of lithium-ions from the graphite electrode [9, 18, 19]. The area covered under the curves of the cyclic voltammogram differs between RVG and AL-AR-25. That may be due to the specific capacity effect that takes place during lithiation-delithiation process as reported previously [18, 19, 23, 24]. According to Fig. 7, RVG shows a high oxidation



Fig. 6 a Voltage profile for initial cycle of RVG, RVG-AL, RVG-AR-25, and AL-AR-25. b Corresponding voltage profile during 1st, 2nd, 50th cycles of RVG. (c) Corresponding voltage profile during 1st, 2nd, 50th cycles of AL-AR-25

region due to its high  $DCC_{sp}$ , whereas the AL-AR-25 shows a high reduction region due to the higher  $CC_{sp}$ . The insert of Fig. 7 shows the cyclic voltammograms obtained for the first 50 cycles of AL-AR-25. It shows of maintaining a fairly an analogous profile over its first 50 cycles due to continuous smooth nature of the lithium ions intercalation and deintercalation process in the graphite anode, as also reported elsewhere [9, 15, 18, 19].

The galvanostatic charge/discharge analysis of the graphite developed in the present study shows their first

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cycle specific discharge capacity as close to the theoretical capacity expected for graphite, while maintaining it above 300 mA h g<sup>-1</sup> even after 50 cycles. Among them, the AL-AR-25 shows a superior performance with a better cycle stability and higher retention capacity. In cyclic voltammograms, the phase transitions behavior is clearly observable in the voltage profiles, by providing evidence for occurrence of the same phase transitions in both raw graphite and developed graphite. Among them, the AL-AR-25 displays the perfect reversibility of the lithiation and delithiation process Fig. 7 Cyclic voltammograms of first cycle obtained for RVG and AL-AR-25 with the insert of cyclic voltammograms of 50 cycles obtained for AL-AR-25



with the largest Li<sup>+</sup> storage capacity. Altogether, the AL-AR-25 shows a promising electrochemical performance for the intended LIB anode application, with the highest retention capacity and the perfect reversibility of the lithiation/delithiation process.

# Discussion

In this study, raw vein graphite was purified by introducing a novel combined alkali roasting and acid leaching method in order to enhance its properties appropriate for the anode application in LIB. Under that, initially NaOH concentrations in the range of 20–40 vol.% were tested for finding the optimum NaOH vol. %, for this alkali roasting method. The starting material of raw vein graphite had a carbon content of 97.5%. The lowest impurity removal efficiency of 47.0% with 98.7% purity were resulted for RVG-AR-40, whereas on the other side the RVG-AR-20 showed the impurity removal efficiency of 52.0% with 98.8% purity. Importantly, the RVG-AR-25 showed the highest impurity removal efficiency of 68.0% also by resulting the highest purity of 99.2%.

The XRD phase analysis evidences for the successfulness of this alkali roasting method for removing impurities such as quartz, pyrite, chalcopyrite/calcite, and siderite partially or completely from raw vein graphite, while preserving the relevant crystal structure of graphite of the space group P6<sub>3</sub> / mmc. Alkali roasting has been identified as an effective purification method for removing gangue minerals such as silicates and sulfides from graphite [30, 31]. Specially, NaOH is preferably used as an alkali additive to remove the

impurities. Impurities react with NaOH during the roasting and a part of them dissolve in water. Moreover, the roasting end products such as Fe and Al can be neutralized by sulfuric acid in the consequent acid-leaching process to form chlorides and dissolve in water. Remarkably, silicates from water-soluble alkali silicates can be eliminated by a simple water-leach [30, 31].

Further, the Raman analysis reveals for having fewer edge defects in RVG-AR-25 than other treated graphite, while SEM study supporting it by displaying the existence of smooth edges. indicating RVG-AR-25 to be the best among the studied alkali roasted graphite for the intended application Finally, the FTIR analysis evidences for occurring considerable modification to the graphite surface and this will be an added advantage for the intended application. In addition, though forming of some additional functional groups during the alkali roasting process on the graphite surface was indicated by the FTIR analysis, this effect was minimal specially in the RVG-AR-25 with compared to other alkali roasted graphite. Based on these findings, the 25 vol. % was selected as the optimum NaOH concentration for alkali roasting of vein graphite.

The HCl acid leaching has been proved to be one of the effective techniques for purifying graphite. Generally, acid leaching has revealed that finely powdered graphite is attacked by the acid and due to the chemical resistance, only a very limited amount of carbon is released into the leach solution. In our previous studies, the optimum HCl concentration for acid leaching of raw vein graphite had been determined as 5 vol. % [6, 7, 32]. By utilizing that finding, the HCl acid leaching process performed under the present study resulted 99.2% of purity with 68.0% of impurity removal efficiency. The phase analysis reveals the limitations faced by the HCl acid leaching to remove impurities that are physically attached or intercalated with graphite. This technique was successful in eliminating the pyrite and siderite but not effective in removing silicate minerals such as quartz as well as sulfate and carbonate. Further, FTIR analysis could not find any evidences for forming additional functional groups hence for any surface modification to graphite.

Acid leaching and alkali roasting methods are both effective purification methods. Performing these methods alone may hinder the achieving of very high carbon around 99.9% purity with minimal metallic impurities, to be used as a successful anode material in LIB. Specially as discussed above, the HCl acid leaching method alone is not effective for removing silicate, sulfates, and carbonates and impurity minerals. However, direct roasting at high temperatures (over 500 to 900 °C) would be effective to remove those silicate impurities [30, 31]. Hence, the acid leaching method and the alkali roasting method should be combined to obtain adequate purity for graphite, aiming for a long cycling life with adequate capacity when used for the anode application in LIB.

Accordingly, the AL-AR-25 graphite was prepared by using the novel combined process introduced in the present study by subjecting graphite already acid leaching process with 5 vol. % of HCl, to the second alkali roasting process with 25 vol. % NaOH. This AL-AR-25 graphite resulted a very high purity of 99.9% with an overall impurity removal efficiency of 96.0%. Accordingly, this combined method is the most effective purification method being eight time more effective than when take the previously mentioned purification methods of acid leaching and alkali roasting alone.

The XRD phase analysis confirmed the presence of high crystallinity with significantly eliminated impurity phases while preserving the required graphite phase. Further, the Raman analysis revealed for fewer edge defects and SEM evidenced for smoother edges. Importantly, the FTIR analysis confirmed the occurrence of considerable modification to the graphite surface and that will be an added advantage for the intended application. By considering this interesting outcome, AL-AR-25 was subjected for further investigations through electrochemical performance investigations, aiming for the intended anode application of in LIB.

According to the galvanostatic charge/discharge analysis, the developed graphite showed their first cycle specific discharge capacity as close to the theoretical capacity expected for graphite, while maintaining it above 300 mA h g<sup>-1</sup> even after 50 cycles. Specially, the AL-AR-25 developed by the combined process showed a greater performance with an improved cycle stability and higher retention capacity. The CV analysis evidenced for the same phase transitions occurring in both raw graphite and the developed graphite. Among them, significantly enhanced reversibility of the lithiation and delithiation process with the largest Li<sup>+</sup> storage capacity could be observed with AL-AR-25. The significantly improved performance of this AL-AR-25 material, which was developed by the novel combined process introduced by the present work, can be correlated to those number of significant characteristics resulted to vein graphite by this novel combined process, as discussed in detailed above.

When compared with the electrochemical performance, the niobium-based materials show a specific capacity of around 175 mA h  $g^{-1}$  [25, 26], while that of vanadium-based materials is 442 mA h  $g^{-1}$ , for three Li<sup>+</sup> intercalations, or 294 mA h g<sup>-1</sup> for two Li<sup>+</sup> intercalations per formula [27, 28]. In contrast to these anode materials, the specific capacity of the developed graphite material in this study lays in between. However, when considering the promising performance already shown by graphite in the intended anode application of lithium-ion rechargeable batteries, it is still worth for further evolving graphite with special attention to those cheaper natural graphite varieties such as vein graphite. This is important specially when compared with those niobium and vanadium-based materials, the vein graphite is abundant, low cost, and rather nontoxic material with high electrical conductivity.

# Conclusion

The research is centered on the combination and optimization of the alkali roasting method and the acid leaching method. Different NaOH concentrations were used to determine the optimum concentration for purification. For HCl acid leaching, an already optimized concertation was utilized. The NaOH concentration primarily affected the alkali roasting process, and based on the preliminary study, 25 vol. % was chosen as the optimum NaOH concentration. The HCl acid leaching resulted a carbon content of 99.2%, and it could be enhanced up to 99.9% after combining it with the NaOH alkali roasting method. Further, while achieving very high purity, the combined purification method could also result in surface modified graphite having smooth edges with few edge defects while preserving the high crystallinity and the relevant crystal structure of graphite of the space group P6<sub>3</sub> / mmc.

The electrochemical performance analyses confirm the enhanced properties with high-rate capacity, high Coulombic efficiency, and low irreversible capacity for the graphite developed by this combined purification method. The specific discharge capacity of the first cycle is 377.6 mA h g<sup>-1</sup> and maintained it over 300 mA h g<sup>-1</sup> with 99.9% Coulombic efficiency, even after 50 cycles. As a whole, the novel combined alkali roasting and HCl acid leaching method introduced in this study have proven its ability for purification

and modification of vein graphite adequately to result in promising electrochemical performance for the anode application in rechargeable Li-ion batteries.

Acknowledgements This work was supported by the General Treasury under a cabinet paper of the Government of Sri Lanka (No: 17/1907/16/038 on 2017.08.09). Members of the National Centre for Advanced Battery Research of National Institute of Fundamental Studies, Sri Lanka, are acknowledged.

#### Declarations

**Conflict of interest** The authors declare no competing interests.

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