



Preparation of sponge-like porous carbon from *Ficus Religiosa* leaf and its K-ion intercalation properties

K. Rajkumar^a, M. Ragupathi^a, Yun Sung Lee^b, R. Kalai Selvan^{a,*}

^a Energy Storage and Conversion Devices Laboratory, Department of Physics, Bharathiar University, Coimbatore 641 046, Tamil Nadu, India

^b Faculty of Applied Chemical Engineering, Chonnam National University, Gwangju 500-757, South Korea

ARTICLE INFO

Keywords:

Biomass carbon
Carbonization
K⁺-intercalation
Specific capacity

ABSTRACT

By one-step carbonization, sponge-like porous carbon was derived from *Ficus Religiosa* leaf. The prepared carbon contains large voids, which will be beneficial for the K⁺-ion intercalation /de-intercalation process. A maximum reversible capacity of 205 mAh.g⁻¹ was obtained at 20 mA.g⁻¹. Further, the porous carbon electrode showed a reversible capacity of 76 mAh.g⁻¹ with 76% capacity retention over 50 cycles at a current density of 50 mA.g⁻¹. Overall, the *Ficus Religiosa* leaf derived biomass carbon can be a good candidate for K⁺-ion intercalating electrodes for energy storage devices.

1. Introduction

The demand for new energy storage technologies has been rapidly increasing, especially to meet large-scale energy requirements. A stationary grid-based storage technology needs abundant reserves that must be economically viable and efficient. Though the present metal-ion battery technology is being dominated by lithium-ion batteries, limited lithium resource and uneven distribution makes it highly uneconomically for stationary grid storage applications [1]. Hence, an alternate, affordable and sustainable energy storage technology is mandatory, where sodium-ion batteries (SIBs) and potassium-ion batteries (PIBs) are gaining interest over the past few years. Among these, the PIBs are considered as the most viable systems since the K⁺ ion exhibits weaker Lewis acidity and has a smaller solvation ion size than Li⁺ and Na⁺ ions [2]. After the identification of K⁺ intercalation into graphite [3], researchers explored different forms of carbon for PIBs [4], where biomass-derived carbon has received significant interest. Since the inherent 3D porous construction provides advantages such as large interlayer spacing with good mechanical stability, large surface area and good thermal stability. Therefore, various biomass carbon derived from bamboo, sugar cane, chitin, bacterial cellulose, loofah, maple leaves, and potato, etc., have been reported so far [4,5]. In this line, the present work reports the use of biomass waste (*Ficus Religiosa* leaf) derived carbon as anodes for PIBs for the first time due to their wider availability under the “waste to wealth” concept. Previously, our group reported the *Ficus Religiosa* leaf derived porous carbon as an electrode for flexible

supercapacitor [6]. Herein we report the K⁺-ion storage properties of biowaste carbon derived from *Ficus Religiosa* leaves as anodes for batteries.

2. Experimental methods and materials

The dead leaves of *Ficus religiosa* were collected from Bharathiar University Campus, Coimbatore, India. The collected dead *Ficus religiosa* leaves were washed with double distilled water, treated with 1 M HCl, dried at room temperature, and made into a fine powder. The leaf powder was carbonized at 900 °C for 3 h in N₂ atm. at the rate of 5 °C/min. The prepared sample is named FR-900 hereafter. The structural properties were investigated by X-ray diffraction (XRD, Bruker D8 Advance) with Cu-Kα radiation in the 2θ range of 10–90°, FT-IR spectrum was collected with JASCO –4000 series, and Raman spectrum was recorded with (HORIBA LabRAM HR) in the range of 800–2000 cm⁻¹ with a Laser excitation of 532 nm. The morphology was observed with a high-resolution transmission electron microscopy (JEOL JEM 2100).

The electrode was prepared by mixing FR-900 (80 wt%), acetylene black (10 wt%) and polyvinylidene fluoride (PVdF) (10 wt%) in the N-methyl-2-pyrrolidone (NMP) and was coated on Cu-foil and dried under vacuum at 100 °C for 12 h. The half cells (2032 coin cell) were assembled in the glovebox with H₂O, and O₂ kept below 0.5 ppm (MBRAUN LABstar) using the punched electrode (16 mm dia. and 1.0 mg) vs K metal. Whatman GF/D glass microfibre filter was used as a separator and 0.8 M KPF₆ dissolved in EC: DEC (1:1 wt%) was used as electrolyte. The

* Corresponding author.

E-mail address: selvankram@buc.edu.in (R. Kalai Selvan).

<https://doi.org/10.1016/j.matlet.2021.130298>

Received 30 April 2021; Received in revised form 4 June 2021; Accepted 18 June 2021

Available online 23 June 2021

0167-577X/© 2021 Elsevier B.V. All rights reserved.

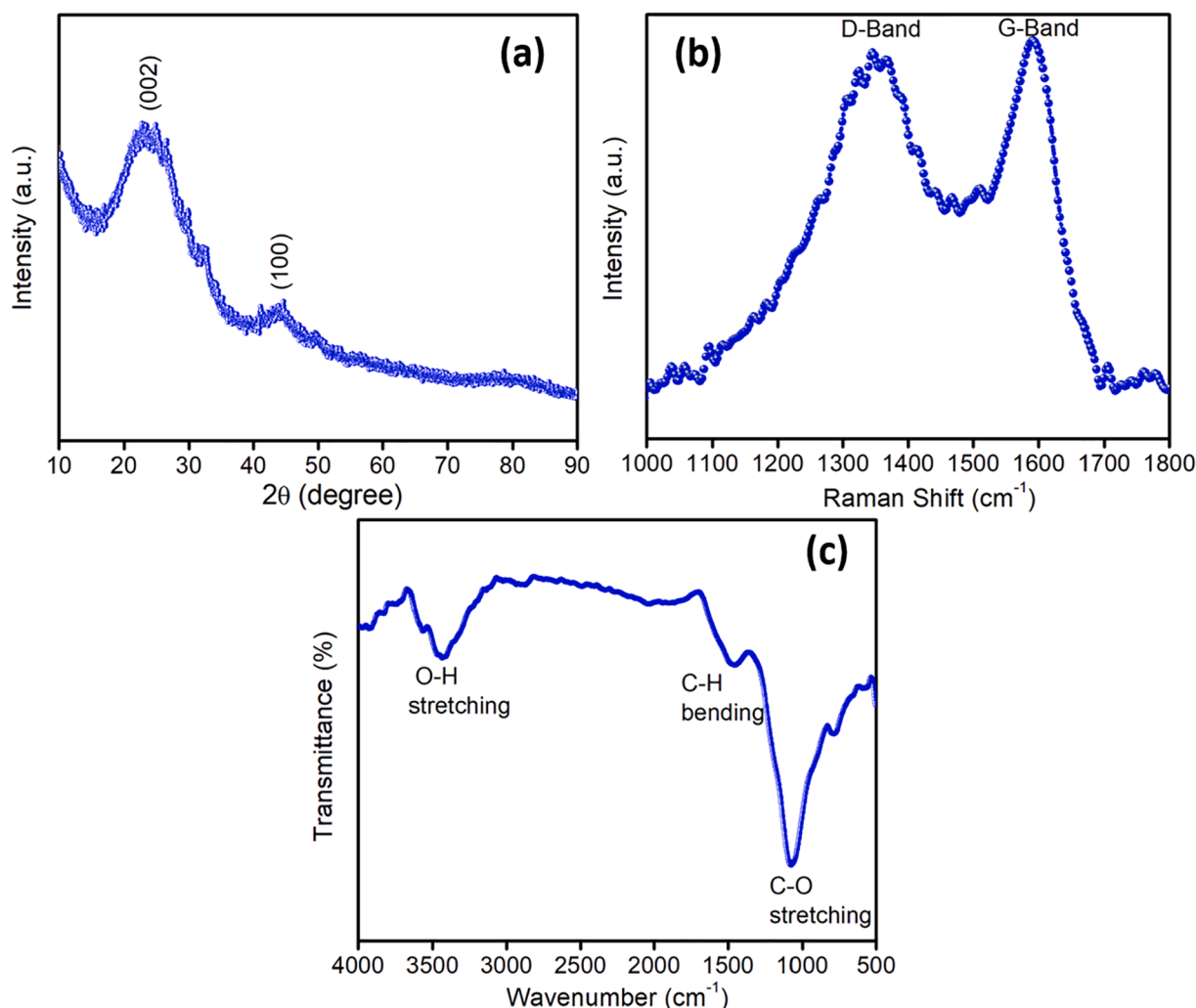


Fig. 1. (a) XRD pattern, (b) Raman spectrum and (c) FT-IR spectrum of FR-900.

(dis)charge cycling tests were performed in the potential range of 0.01–3.00 V vs K/K⁺ with a WonATech battery cycler (WBCS 3000L). The cyclic voltammograms (CV) was collected with a Biologic (VSP Model) electrochemical workstation.

3. Results and discussion

The XRD pattern of FR-900 (Fig. 1(a)) shows two prominent broad diffraction peaks between 20 – 30° and 40 – 50° corresponding to (200) and (100) planes of graphitic carbon. XRD pattern matches with the graphite (JCPDS No. 41–1487) [7]. The broad peak around 23.7° indicates that the ordering exists only for few nanometers. The peak at 44° corresponds to inter and intralayer scattering in the graphene stacks, which indicate the presence of graphitic structure [8,9]. The Raman spectrum (Fig. 1(b)) depicts two peaks around 1346 and 1590 cm⁻¹ in the measured range (1000–1800 cm⁻¹). The peak at 1346 cm⁻¹ corresponds to defective (D) band, which is due to the vibrations of disordered carbon atoms (A_{1g} symmetry) from a defective graphitic structure, or the edges of the graphite sheets, and the peak at 1590 cm⁻¹ corresponds to the graphitic (G) band of C–C in-plane stretching vibrations of sp² hybridized graphitic carbon atoms (E_{2g} symmetry) [8]. The estimated intensity ratio (I_D/I_G) is 0.98, which is lesser than 1, reveals the presence of lesser defects in the carbon. The FT-IR spectrum (Fig. 1(c))

displays the bands around 1082, 1489 and around 3458 cm⁻¹, corresponding to the C–O stretching, C–H bending, and O–H stretching vibrations, respectively. The available functional groups act as binding sites for K⁺ ions during intercalation [10].

The morphological features of the FR-900 are studied at different magnifications using HRTEM, and the images are shown in Fig. 2 (a–c). It reveals that the particles are highly porous, with sponge-like morphology having large voids. It is believed that the observed large porous structures with thin carbon layers will be highly beneficial for K⁺-ion (de)intercalation. The observed concentric rings (Fig. 2 (d)) in the SAED pattern confirms the polycrystalline nature of the prepared carbon.

To study the electrochemical performances of the FR-900 electrode (Fig. 3), CV tests were performed in the potential range of 0.01 and 3 V vs K/K⁺ at 0.05 mV.s⁻¹ (Fig. 3a). In the first cycle, a small bump in the voltage range of 0.4 V to 1 V vs K/K⁺ is observed during the negative scan due to the formation of SEI layer on the surface of the electrode [11], and this is the reason for the observed high initial capacity with low coulombic efficiency in the GCD curve (Fig. 3b). The observed reduction peak at ~ 0.3 V vs K/K⁺ elucidates the adsorption of K⁺-ions on the surface of the carbon particles. The region below 0.3 V vs K/K⁺ infers the intercalation of K⁺-ions, and the oxidation peak at ~ 0.5 V vs K/K⁺ corresponds to the removal of adsorbed K⁺-ions from the carbon

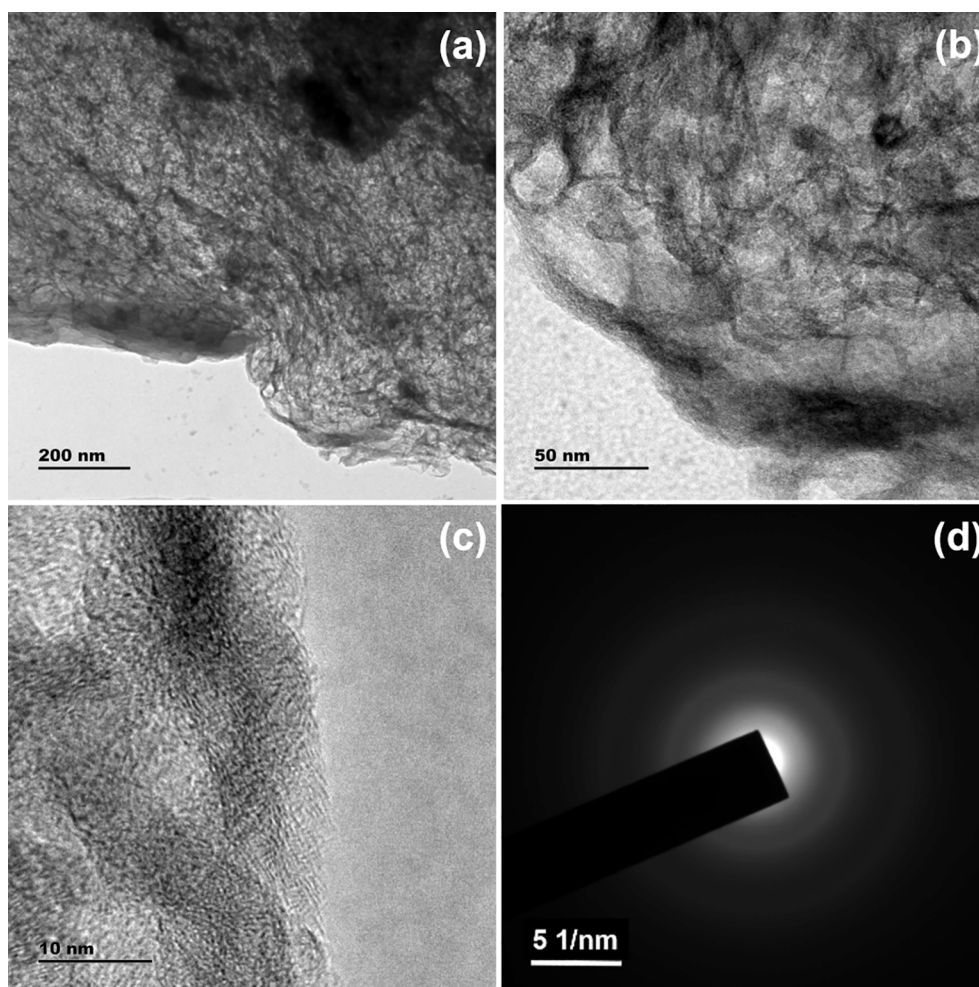


Fig. 2. HRTEM images at different magnifications (a-c) and the (d) SAED pattern Fig. 2 of FR-900.

particles [8].

To validate the K^+ -intercalation properties, a galvanostatic-charge discharge (GCD) study is performed in the voltage range of 0.01 V to 3 V vs K/K^+ . Fig. 3(b) shows the first five GCD curves of FR-900 cycled between 0.01 V and 3 V (vs. K/K^+) at a current density of 20 mA g^{-1} (Fig. 3(b) inset shows the GCD curves excluding the first cycle). The first potassiation capacity is 625 mAh.g^{-1} , but the observed de-potassiation capacity is $\sim 200 \text{ mAh.g}^{-1}$, a large difference in capacity and low coulombic efficiency during the first cycle is attributed to the formation of the SEI layer [11]. During the subsequent cycles, the reversible characteristics of the materials are observed. To assess the dynamics performance, the rate capability was studied at different current densities from 20 to 280 mA g^{-1} (inset: Fig. 3c). At low current densities, the capacity is decreasing with an increase in cycle number. Above 50 mA.g^{-1} the capacities are found to be stable. At 20 mA.g^{-1} for the second cycle, the capacity was 190 mAh.g^{-1} . The average capacity at 50, 100, 160, 200, 260 and 280 mA.g^{-1} are 100, 68, 50, 40, 30 and 25 mAh.g^{-1} , respectively. Average capacity at 20 mA g^{-1} done after 280 mA g^{-1} reached 125 mAh.g^{-1} . At low current densities, there is a loss in capacity with less coulombic efficiency. In contrast, at higher current densities, the discharge capacity is found to be stable with good coulombic efficiency. While increasing the current density from lower to higher, there is a minimal decrease in capacity. Fig. 3c depicts the cyclic stability of the cells measured at 50 mA g^{-1} for 50 cycles. It can be seen that there is 76% of capacity retention after 50 cycles to the second cycle. The coulombic efficiency was almost 100% except for the first cycle. The discharge capacity can be further improved by optimizing the

carbonisation temperature and incorporating heteroatoms like O, N and S in future [4].

4. Conclusions

In the present work, the biomass-based sponge-like porous carbon derived from *Ficus religiosa* dead leaf is reported as the anodes for PIBs. The porous carbon was prepared by the direct carbonization method at 900°C in N_2 atm. The prepared carbon is found to possess large voids with porous structure, as revealed from HRTEM. The initial irreversible capacity of 625 mAh.g^{-1} was obtained in the first cycle at 20 mA g^{-1} . A reversible capacity of 205 mAh.g^{-1} was obtained in the second cycle. The porous carbon electrode showed a reversible capacity of 76 mAh.g^{-1} with 76% of capacity retention over 50 cycles at a current density of 50 mA g^{-1} . The prepared biomass-based porous carbon derived from *Ficus religiosa* is very interesting as it exhibits a large void and it is highly porous with a polycrystalline structure. This is very beneficial for the large K^+ ions to intercalate/de-intercalate easily.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

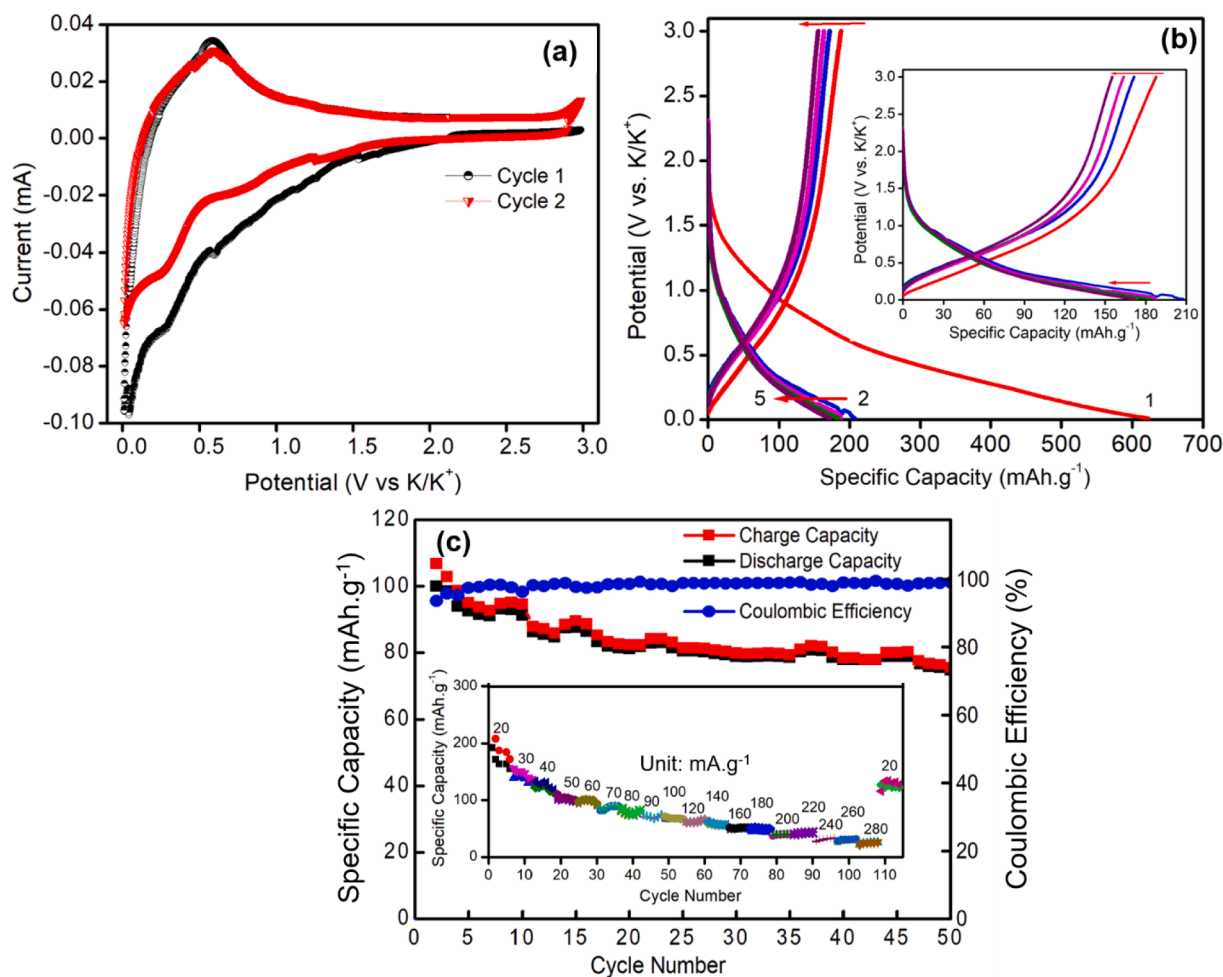


Fig. 3. (a) Cyclic voltammogram at 0.05 mV.s^{-1} , (b) GCD curves of 1st five cycles at 20 mA.g^{-1} (inset: except 1st cycle), (c) cycling stability measured at 50 mA.g^{-1} (inset: rate capability) of FR-900 cells.

Acknowledgements

Dr R.K.Selvan greatly acknowledges to Council of Scientific and Industrial Research, New Delhi (03(1421)/18EMR-II dated 04.06.2018), DST-SERB (CRG/2018/001995 dated 09.04.2019) for the financial support and the DST-FIST program for the establishment of the Glove-box facility. The authors would like to thank the UGC-CPEPA Centre, BU for extending the Raman instrumental facility. Prof. Y.S.Lee gratefully acknowledge the financial support from a National Research Foundation of Korea (NRF) grant funded by the Korean government (Ministry of Science, ICT & Future Planning) (No. 2019R1A4A2001527).

References

- [1] D. Larcher, J.-M. Tarascon, Towards greener and more sustainable batteries for electrical energy storage, *Nat. Chem.* 7 (1) (2015) 19–29.
- [2] S.-S. Fan, H.-P. Liu, Q. Liu, C.-S. Ma, T.-F. Yi, Comprehensive insights and perspectives into the recent progress of electrode materials for non-aqueous K-ion battery, *J. Mater. Chem.* 6 (2) (2020) 431–454.
- [3] Z. Jian, W. Luo, X. Ji, Carbon electrodes for K-ion batteries, *J. Am. Chem. Soc.* 137 (36) (2015) 11566–11569.
- [4] X. Yuan, B.o. Zhu, J. Feng, C. Wang, X. Cai, R. Qin, Recent advance of biomass-derived carbon as anode for sustainable potassium ion battery, *Chem. Eng. J.* 405 (2021) 126897, <https://doi.org/10.1016/j.cej.2020.126897>.
- [5] T.J. Yokokura, J.R. Rodriguez, V.G. Pol, Waste biomass-derived carbon anode for enhanced lithium storage, *ACS Omega* 5 (31) (2020) 19715–19720.
- [6] S.T. Senthilkumar, R.K. Selvan, Flexible fiber supercapacitor using biowaste-derived porous carbon, *ChemElectroChem* 2 (8) (2015) 1111–1116.
- [7] J. Yang, Z. Ju, Y. Jiang, Z. Xing, B. Xi, J. Feng, S. Xiong, Enhanced capacity and rate capability of nitrogen/oxygen dual-doped hard carbon in capacitive potassium-ion storage, *Adv. Mater.* 30 (4) (2018) 1700104, <https://doi.org/10.1002/adma.201700104>.
- [8] K. Rajkumar, C. Sudakar, Candle soot carbon nanoparticles as high-performance universal anode for M-ion ($M = \text{Li}^+$, Na^+ and K^+) batteries, *J. Power Sources* 458 (2020) 228064, <https://doi.org/10.1016/j.jpowsour.2020.228064>.
- [9] C. Zhao, H. Li, Y. Zou, Y. Qi, Z. Jian, W. Chen, Low-cost carbon materials as anode for high-performance potassium-ion batteries, *Mater. Lett.* 262 (2020) 127147, <https://doi.org/10.1016/j.matlet.2019.127147>.
- [10] A.K. Nanjundan, R.R. Gaddam, A.H. Farokh Niaei, P.K. Annamalai, D.P. Dubal, D. J. Martin, Y. Yamauchi, D.J. Searles, X.S. Zhao, Potassium-ion storage in cellulose-derived hard carbon: the role of functional groups, *Batteries Supercaps.* 3 (9) (2020) 953–960.
- [11] S. Zhang, M.S. Ding, K. Xu, J. Allen, T.R. Jow, Understanding solid electrolyte interface film formation on graphite electrodes, *Electrochem. Solid State Lett.* 4 (12) (2001) A206, <https://doi.org/10.1149/1.1414946>.