

Structure and electrochemical sodium storage properties of hard carbon doped with molybdenum

N.S. Saenko*, V.V. Zheleznov, D.P. Opra

*Institute of Chemistry FEB RAS,
159, Prospekt 100-letiya Vladivostoka, Vladivostok, 690022, Russia*

**E-mail: saenko@ich.dvo.ru.*



www.ichdvo.ru

Institute of Chemistry FEB RAS

Sodium has become a cheap alternative to lithium due to relatively simple production methods and high availability [1, 2]. Hard carbon is the most promising material for use as negative electrodes in sodium-ion chemical current sources, as it comes from natural renewable compounds, has a relatively low cost, and its production has a minimal impact on the environment [3]. However, hard carbon anode material in sodium ion batteries (SIBs) has low capacity at high charging currents [4]. Heteroatomic doping is a widespread way to improve the characteristics of hard carbon materials. For example, simultaneous doping of hard carbon with nitrogen and sulfur leads to an enlarging interlayer distance and an increasing number of defects, which enhances the electrode kinetics and electronic conductivity of SIBs [5, 6]. Several papers report doping hard carbon with molybdenum [7, 8, 9, 10, 11]. However, the complexity of synthesis and the production cost of anode materials primarily determinates their industrial use perspectives for application in SIBs. The paper investigates the structure and electrochemical sodium storage properties of materials prepared by annealing at different temperatures of industrial viscose fibers doped with molybdenum.

The original viscose industrial thread (manufactured by the Svetlogorsk plant of artificial fibers, Republic of Belarus) have been washed with 0.1 N HCl and deionized water. Molybdenum salts have been applied to the fiber by impregnation followed by air drying to remove free water. Carbonization have been carried out in a tube furnace in an argon atmosphere. Temperature rise rate was 3-10 °C/min. The temperature was raised stepwise with exposure at temperatures of 220, 280 and 350 °C, in zones where, according to thermographic curves, the processes of dehydration, depolymerization, decarbonylation proceed [29], to a final temperature in the range of 360–1300 °C.

The X-ray diffraction patterns of materials have been recorded on the D8 ADVANCE diffractometer (Bruker, Germany) in the Bragg-Brentano setting with a CuK α source ($\lambda = 0.15417$ nm). The measurements have been carried out in the angular range 2θ from 5 to 90° with a step of 0.02° and a counting time of 10 s per step.

The electrochemical characteristics of doped solid carbon have been studied by cyclic voltammetry (CV) and galvanostatic charge-discharge in the potential range of 2.5–0.005 V. Working electrodes have been prepared according to standard spreading technology using a mixture (87:13 by weight) of solid carbon and Tuball Bat NMP substance produced by OCSiAl in 1-methyl-2-pyrrolidone. The aluminum foil pre-treated in a dilute hydrochloric acid solution have been used as the current collector. The electrodes have been dried at 60°C to a constant weight, pressed at 800 kg/cm², and heat treated in vacuum at 110°C for 12 h. Electrochemical cells have been assembled in a dried box in an argon atmosphere. Sodium metal served as the counter and reference electrode, and Whatman glass fiber material have been used as a separator. A 1 M solution of NaClO₄ in propylene carbonate with the addition of 5 vol.% fluoroethylene carbonate have been used as an electrolyte.

There are two broad intensive peaks at ≈ 24 and 43° in the X-ray diffraction profiles of all materials (fig. 1). Low-intensity peaks corresponding to molybdenum compounds are noticeable in the diffraction profile of material prepared at 630°C. At an annealing temperature of 950°C, there are characteristic reflections of molybdenum oxide MoO₃. At higher annealing temperatures (1050 and 1300°C), peaks of molybdenum carbides are registered. The X-ray scattering profiles of all the materials (fig. 1) can be approximated by the sum of Lorentzians and background scattering in the form of a fourth-degree polynomial in $1/2\theta$, reflecting the contributions to the background scattering profile (due to small-angle scattering, scattering by disordered atoms, scattering by air molecules, and other factors) [12]. In all experimental diffraction patterns, one can distinguish reflections (002), (10), (004), (11) characteristic of turbostratic multilayer nanographenes with maxima near 2θ of 23, 42, 49, and 80°, respectively [13, 14]. Besides, in the approximations of materials prepared at 630 and 950°C, one can distinguish the Lorentzian with a maximum at $2\theta \sim 19^\circ$, the so-called γ -peak [15, 16, 17]. Additional narrow components at $2\theta \sim 26, 32, 37, 40, 62, 75^\circ$ in the approximation can be attributed to scattering on nanocrystallites of molybdenum oxide and molybdenum carbides.

The interatomic and interlayer spacing, average lateral size and thickness of ordered carbon regions have been estimated using the Debye-Scherrer formula and Bragg's law [14, 18, 19]. The ordered carbon regions in the materials prepared at 630°C have an average lateral size of 1.2 nm. Materials prepared at temperatures higher than 950°C have more extended areas of the ordered carbon network. It should be noted that the distance between ordered carbon layers in all samples significantly exceeds the interlayer distance in turbostratic carbon [20, 21]. This fact may indicate that there are functional groups associated with the carbon network in the interlayer space of these samples [22], or interstitial atoms and molecules [23]. The distance between the carbon layers in the materials decreases in the annealing temperature range from 630 to 1050°C and then increases in the sample annealed at 1300°C. Among all materials, one prepared at 950°C has the maximum number of layers and the maximum distance between the carbon layers in the particles, and therefore it was chosen for testing as a material for negative electrodes in sodium-ion batteries.

The hard-carbon material has been studied by cyclic voltammetry (CV) and galvanostatic charge-discharge tests. Fig. 2a represents the five initial CV cycles recorded at a potential sweep rate of 0.1 mV/s for a sodium half-cell with working electrode from the hard carbon material annealed at 950°C. There is a pronounced peak near 1.0 V in the cathode region of the first CV curve (fig. 2a). The mentioned peak does not have a corresponding response in the anode region as well as does not repeated on the curves of subsequent cycles. The origin of this peak is explained by irreversible reactions at the electrode surface and the resultant formation of a solid electrolyte interphase layer [24, 25]. The experimental data are in good agreement with a sodiation mechanism proposed for hard carbon in the literature [26]. In this way, peaks centered near 0.6, 0.1, and 0.01 V correspond to the staged process of sodium accumulation in the anode material. The anode region of all the voltammograms shows a wide peak with a maximum near 0.25 V. It should be noted that by the third cycle, the intensity of this peak increases. Such behavior is typical for hard carbon [27, 28] and is caused by changes in structure and texture during sodium uptake/release. The electrochemical process stabilizes starting from the fourth cycle.

The initial voltage profiles for the sodium half-cell based on hard carbon material annealed at 950°C were obtained at a current density of 25 mA/g (fig. 2). There are several regions on a charge curve indicating a multi-stage electrochemical process. The latter agrees well with the CV data. The corresponding discharge profile shows a pronounced plateau at 0.1 V. The specific capacity values recorded during the first charge and discharge are approximately 455 and 230 mAh/g, respectively, and the irreversible losses are about 225 mAh/g. The subsequent tenfold cycling (fig. 2b, inset) reflects the stabilization of the electrochemical process with a reversible capacity of around 240 mAh/g. Thus, the electrochemical measurements have shown the promise of obtained materials as anode materials for sodium-ion batteries.

The study was supported by the Ministry of Science and Higher Education of Russia (state assignment № 0205-2021-0004 and № 0205-2021-0001). Electro-chemical studies were carried out within the framework of the grant № 22-23-00912 from the Russian Science Foundation.

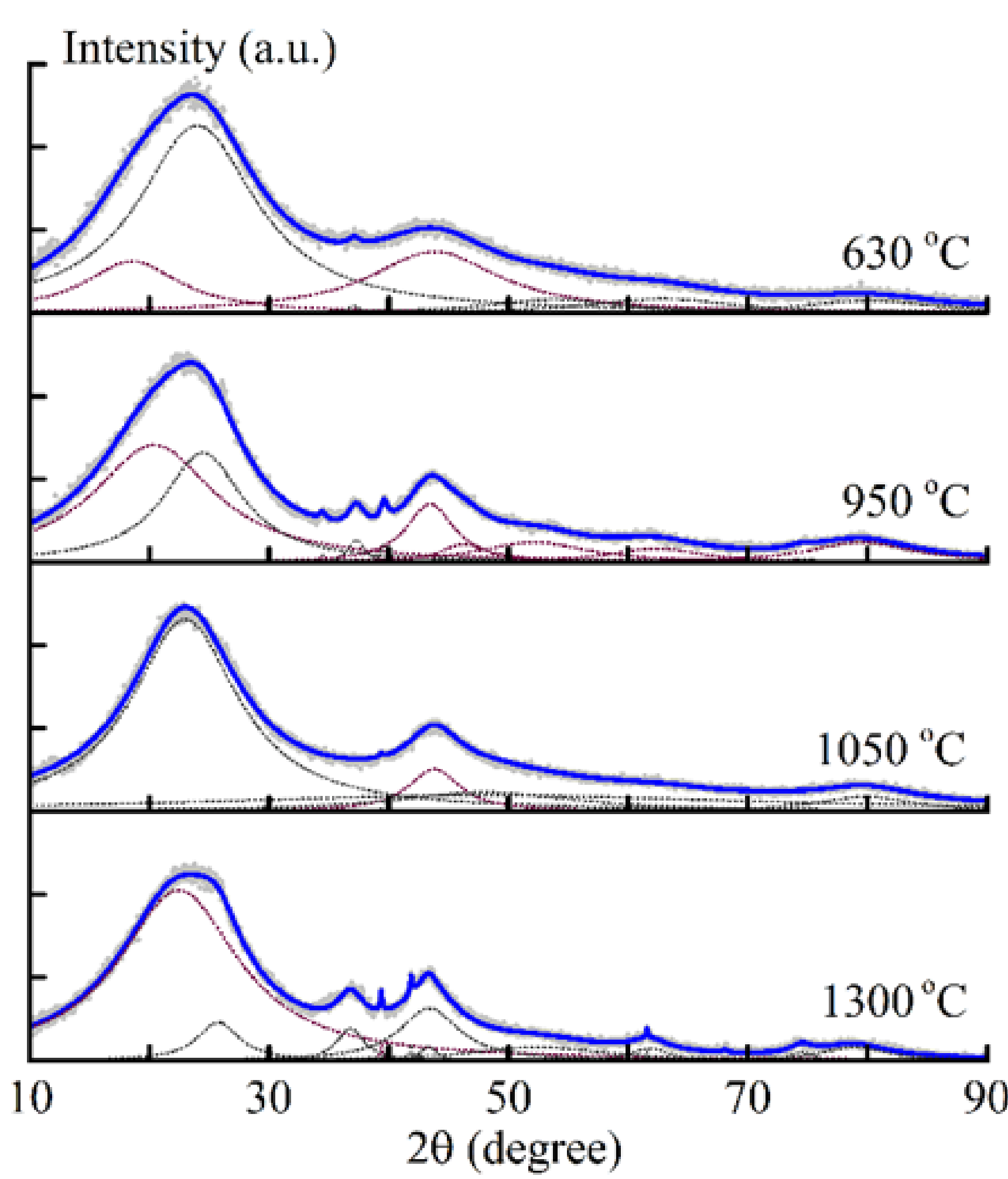


Fig. 1. Approximation of X-ray diffraction patterns of materials prepared from viscose fiber doped with molybdenum at different annealing temperatures after subtracting the contribution of the background scattering.

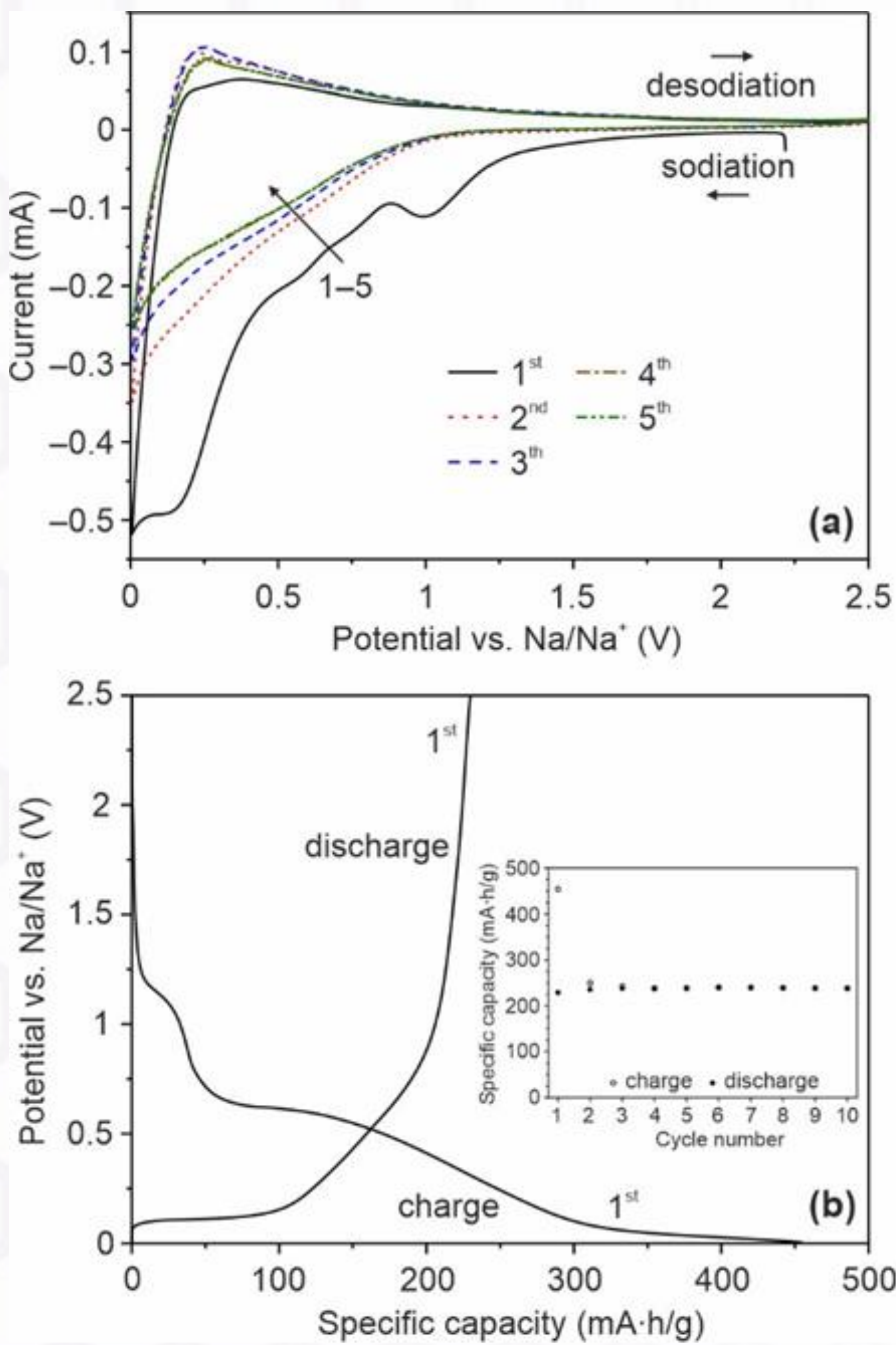


Fig. 2. (a) Curves of cyclic voltammetry at 0.1 mV/s and (b) charge-discharge profiles of the first cycle at 25 mA/g for hard carbon material (the inset shows the results for ten cycles).

References

1. F. Xie et al. Prog. Energy **2**(2020)042002.
2. J. Ma et al. J. Phys. D: Appl. Phys. **54**(2021)183001.
3. Thompson M., Xia Q., Hu Z., Zhao X.S. Mater. Adv. **18**(2021)5881.
4. W. Wang et al. J. Mater. Chem. A. **6**(2018)6183.
5. H. Hou et al. Adv. Energy Mater. **7**(2017)1602898.
6. D. Xu et al. Adv. Energy Mater. **6**(2016)1501929.
7. L. David, R. Bhandavat, G. Singh. ACS Nano. **8**(2014) 1759–1770.
8. C. Zhu et al. Angew. Chemie. **126**(2014)2184.
9. Q. Xia, Q. Tan. Patent CN №106910884.
10. L. Zeng et al. Polymers. **12**(2020)2134.
11. Y. Hao, C. Wang. Molecules **25**(2020)1014.
12. C. Sisu et al. Dig. J. Nanomater. Bios. **11**(2016)435.
13. N. Iwashita et al. Carbon **42**(2004)701.
14. B.E. Warren. Phys. Rev. **59**(1941)693.
15. R.K. Boruah et al. J. Appl. Crystallogr. **41**(2008)27.
16. L. Biennier et al. Carbon **47**(2009)3295.
17. N.S. Saenko, A.M. Ziatdinov. Mater. Today: Proc. **5**(2018)26052.
18. P. Scherrer. Gottinger Nachrichten Math. Phys. **2**(1918)98.
19. W.H. Bragg, W.L. Bragg. Proc. R. Soc. London. Ser. A. **88**(1913)428.
20. J. Biscoe, B.E. Warren. J. Appl. Phys. **13**(1942)364.
21. A. Oberlin, S. Bonnamy, K. Oshida. Tanso. **224**(2006)281.
22. A.M. Ziatdinov, N.S. Saenko, P.G. Skrylnik. **65**(2020)133.
23. M.S. Dresselhaus, G. Dresselhaus. Adv. Phys. **30**(1981)139.
24. K. Xu et al. Front. Chem. **7**(2019)733.
25. Z. Zhu et al. J. Mater. Chem. A. **6**(2018)1513.
26. Z.V. Bobyleva et al. Electrochim. Acta. **354**(2020)136647.
27. L. Wu et al. ChemElectroChem. **3**(2016)292.
28. P. Yu et al. J. Colloid Interface Sci. **582**(2021)852.
29. V.V. Litvinskaya et al. Solid Fuel Chem. **2**(2003)51.