

Energy & Environmental Science

Volume 18
Number 16
21 August 2025
Pages 7723–8094

rsc.li/ees



ISSN 1754-5706

COMMUNICATION

Enis Oğuzhan Eren, Paolo Giusto *et al.*
An enhanced three-stage model for sodium storage in hard
carbons

Cite this: *Energy Environ. Sci.*, 2025, 18, 7859Received 18th December 2024,
Accepted 21st May 2025

DOI: 10.1039/d4ee06029f

rsc.li/ees

A comprehensive understanding of the sodium storage mechanism in hard carbons is essential for developing more efficient anode materials and improving the electrochemical performance of sodium-ion batteries. The mechanism has been the subject of ongoing debate, particularly regarding the role of intercalation, which we found to be insignificant in our study. By combining electrochemical analyses with *operando* characterization techniques, we propose a refined model of sodium storage in hard carbons. Our findings reveal a three-stage process: first, a fast-capacitive mechanism dominates in the slope region; second, a transition phase occurs at the early plateau, where faradaic processes become significant at the carbon micropore inner surface; and finally, micro- and slit-pore filling becomes dominant at the late plateau, driven by a multilayer-like deposition of quasimetallic sodium in the micropores. We believe this refined mechanism promotes a better understanding of the sodium storage mechanism in hard carbons and provides the basis for the rational design of carbon anode materials with superior performance for sodium-ion batteries.

An enhanced three-stage model for sodium storage in hard carbons†

Enis Oğuzhan Eren,^{ib}*^a Evgeny Senokos,^a Ernesto Scoppola,^{ib}^b Zihan Song,^c Markus Antonietti^{ib}^a and Paolo Giusto^{ib}*^a

Broader context

The global transition to renewable energy and electric transportation depends on the development of efficient, sustainable, and cost-effective energy storage solutions. Sodium-ion batteries are emerging as a promising alternative to lithium-ion batteries, with hard carbons gaining attention as anode materials due to their unique structural properties. These properties facilitate sodium storage through mechanisms that differ from lithium intercalation in graphite. By combining electrochemical analyses with *operando* small-angle X-ray scattering, wide-angle X-ray scattering, and Raman spectroscopy, we reveal a refined three-stage adsorption-accumulation-filling model: (1) a fast-capacitive mechanism dominates in the slope region, (2) a transition phase occurs at the early plateau, where faradaic processes become significant at the carbon micropore inner surface, resulting in quasimetallic sodium monolayer formation, and (3) micro- and slit-pore filling becomes dominant at the late plateau, driven by a multilayer-like clustering of quasimetallic sodium in the micropores. Additionally, we demonstrate that sodium intercalation is unlikely to play a critical role in the overall sodium storage mechanism. By addressing challenges in understanding the electrochemical evolution, this work contributes to the development of more sustainable energy storage technologies and advances battery research.

1. Introduction

The sodium storage mechanism in hard carbons (HCs) has long been studied due to their potential for commercial-scale sodium-ion batteries (SIBs).^{1–3} These materials feature a localized short-range arrangement, often referred to as a pseudo-graphitic structure, that is rich in defect sites, and forms a large fraction of isolated closed pores.^{4–6} The sodium storage mechanism in hard carbon differs significantly from the lithium storage mechanism

in graphite, necessitating unique material properties for being effective in SIBs. The similarities drawn from lithium-ion battery (LIB) chemistry do not directly apply to SIBs due to the absence of a stable sodium-carbon intercalation compound.⁷ Theoretical calculations propose a stable sodium-carbon compound NaC₆₄ (35 mA h g⁻¹), which represents an insignificant capacity compared to LiC₆ (372 mA h g⁻¹), and therefore, challenges the feasibility of intercalation-based sodium storage mechanism in such materials.⁸ Consequently, the emphasis is shifting towards pore engineering,⁹ particularly by controlling the ratio of open to closed pores to enhance plateau capacity and overall sodium storage performance,^{10–12} making it essential to understand the underlying sodium storage mechanisms in order to enable SIBs to compete with state-of-the-art LIBs.

The widely accepted sodium storage mechanism in hard carbon materials is centered around the adsorption-intercalation/pore-filling model, which is typically divided into two main potential

^a Department of Colloid Chemistry, Max Planck Institute of Colloids and Interfaces, Potsdam 14476, Germany. E-mail: enis.eren@mpikg.mpg.de, paolo.giusto@mpikg.mpg.de

^b Department of Biomaterials, Max Planck Institute of Colloids and Interfaces, Potsdam 14476, Germany

^c Department of Engineering Science, University of Oxford, Oxford OX1 3PJ, UK

† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d4ee06029f>





Fig. 2 (a) SAXS profile of the HC showing Porod's and the microporous region, along with the fitting of a high-confidence model introduced for non-graphitic carbons. (b) Intensity profile of the mid- q region during sodiation and desodiation processes, describing the intensity change that vastly occurs during the late plateau phase. (c) Schematic describing the average interlayer distance, pore diameter, and correlation length. (d) Variation in $\Delta\bar{\rho}$ during sodiation, revealing pore-filling mostly pronounced at the late plateau region. (e) A heat map visualizes ten different regions in the same electrode for the reproducibility of the analysis. Regions have a similar trend in normalized $\Delta\bar{\rho}$ (smoothed) variation. (f) Plot of $\Delta\bar{\rho}$ with the diffusion coefficients obtained from GITT analysis versus the potential. (g) A close-up view of the trends in $\Delta\bar{\rho}$ and the diffusion coefficient at the early and late plateau.

studies.^{30,47} As the applied potential increases, ions interact with the pore surfaces and recombine with the stored counter-electrons, transitioning into a near-neutral charge state ($\text{Na}^+ \rightarrow \text{Na}^\alpha$, where $\alpha < 1$) during the early plateau, forming a monolayer film. When this monolayer is saturated, storage transits to the late plateau behavior where multi-layer structures are energetically accessed. This progression can be described analogously using the Brunauer–Emmett–Teller (BET) theory of gas physisorption, where increasing gas pressure drives the transition from monolayer to multilayer adsorption. During the late plateau, we propose that sodium ions form

quasi-metallic clusters, reducing local charge repulsion and enabling denser multilayer-like packing, which corresponds to the observed increase in the diffusion coefficient.⁴⁷ This process resembles again the saturation of adsorption sites in BET theory, where multilayer adsorption culminates in pore condensation. In the sodium-ion system, multilayer-like clustering enables denser configurations, allowing more ions to occupy the internal pores. This dynamic continues until the slit- and micro-pores are filled. Beyond this point, sodium metal plating at the outside of the carbon pore system and particles initiates below 0 V (vs. Na^+/Na).³⁰ Therefore, the electrode is also





Fig. 3 (a) Raman spectra of the HC during sodiation and desodiation, revealing slight intensity changes in the D-band and a sharp shift in the G-band. (b) A heat map with normalized intensity visualizes the pronounced shift in the G-band during sodiation and desodiation. (c) *Operando* WAXS pattern, showing the C(002) peak of hard carbon alongside contributions from the Al current collector and a broad, insignificant background from the electrolyte. The C(002) peak is resolved and isolated via peak fitting, with no overlap from electrolyte contributions. (d) WAXS patterns during sodiation and desodiation, revealing no shift in the C(002) but a slight decrease in intensity at the beginning of the electrochemical process. (e) Normalized heat map of the deconvoluted C(002) peak visualizes no pronounced shift during the electrochemical processes.

increasing saturation of these surfaces. The final stage involves the reduction of additional sodium atop the initial monolayer, forming a multilayer-like cluster within the micro- and slit-pores. The formation of these clusters reduces the effective charge repulsion between sodium ions by lowering the local positive charge density. As a result, the migration of additional sodium ions into the pores becomes energetically more favorable, facilitating improved ion mobility. This transition leads to a relative stabilization and an increase in the diffusion coefficient. The multilayer-like deposition process contributes about 31% of the overall capacity (late plateau). *Operando* SAXS measurements support this mechanism, showing a sharp

decrease in electron density differences due to the significant increase in sodium volume ratio within the pores.

It is worth noting that material modifications such as heteroatom doping and electrolyte composition can influence sodium storage behavior. For instance, nitrogen doping introduces additional defect sites and heteroatom functionalities, which can facilitate sodium accumulation and pore filling, leading to an increased plateau capacity.⁵⁶ Similarly, the nature of the electrolyte affects the sodium ion solvation environment: ether-based electrolytes, with weaker solvation and lower desolvation barriers, enhance ion transport and favor more efficient pore-filling processes, while ester-based electrolytes can





Fig. 4 The summary of the main findings regarding the *operando* investigations, along with a galvanostatic sodiation curve, *i.e.*, the trends in sodium-ion diffusion coefficients obtained from GITT (in red, plotted against capacity rather than potential, as in Fig. 1g, for comparative analysis), the change in electron density differences ($\Delta\rho$) of micropores (in blue), the G-band peak of the carbon (in green), and the scattering vector (q) of the C(002) peak (in purple).

hinder these steps due to stronger solvation energy.^{4,57,58} Nevertheless, these variations primarily modulate the energetics and kinetics of each storage stage without altering the overall sequential mechanism. Based on those, we propose the adsorption-accumulation-filling model as a more accurate and contemporary framework for describing the sodium storage mechanism in hard carbons (Fig. 4).

3. Conclusions

Combining electrochemical characterizations with *operando* SAXS, WAXS, and Raman spectroscopy provides a refined understanding of sodium storage mechanisms in hard carbons. The proposed three-stage model identifies a capacitive mechanism occurring in the slope region, transitioning through an early plateau with a decrease in sodium-ion mobility, and culminating in a dominant micropore-filling mechanism during the late plateau, as indicated by *operando* SAXS. *Operando* Raman spectroscopy illustrates changes in the G-band position due to strong ionic Na-C interactions, while *operando* WAXS highlights the absence of visible intercalation evidences. We believe that the current model will serve as a basis for designing electrode materials with superior performance by fine-tuning the porous structure of hard carbons and correlating it to the relevant electrochemical energy storage steps.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This research has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme, MoMa-STOR (Grant agreement No: 951513). The authors thank the Max Planck Society for funding. The authors acknowledge the Max Planck Institute of Colloids and Interfaces and the Helmholtz Zentrum Berlin for the allocation of beamtime under proposal number 232-12432-CR. Open Access funding provided by the Max Planck Society.

References

- 1 J. W. Choi and D. Aurbach, Promise and reality of post-lithium-ion batteries with high energy densities, *Nat. Rev. Mater.*, 2016, **1**(4), 16013.
- 2 H. M. Zhang, Y. X. Huang, H. Ming, G. P. Cao, W. F. Zhang, J. Ming and R. J. Chen, Recent advances in nanostructured carbon for sodium-ion batteries, *J. Mater. Chem. A*, 2020, **8**(4), 1604–1630.
- 3 X. Dou, I. Hasa, D. Saurel, C. Vaalma, L. Wu and D. Buchholz, *et al.*, Hard carbons for sodium-ion batteries: Structure, analysis, sustainability, and electrochemistry, *Mater. Today*, 2019, **23**, 87–104.
- 4 E. O. Eren, E. Senokos, Z. Song, B. Mondal, A. Perju and T. Horner, *et al.*, Hard carbon from a sugar derivative for next-generation sodium-ion batteries, *Mater. Horiz.*, 2025, **12**(3), 886–898.
- 5 Y.-J. Xu, Y.-Y. Wang, Z.-Y. Gu, C.-S. Zhao, X.-L. Wu, S. R. P. Silva and B.-H. Hou, Cellulose-grafting boosted pyrolysis nucleation: Achieving low-temperature construction of hard carbon anodes with long low-voltage plateau and ultrafast Na storage kinetics, *Energy Storage Mater.*, 2025, **75**, 104031.
- 6 M.-Y. Su, K.-Y. Zhang, E. H. Ang, X.-L. Zhang, Y.-N. Liu and J.-L. Yang, *et al.*, Structural regulation of coal-derived hard



- carbon anode for sodium-ion batteries via pre-oxidation, *Rare Met.*, 2024, **43**(6), 2585–2596.
- 7 H. Moriwake, A. Kuwabara, C. A. J. Fisher and Y. Ikuhara, Why is sodium-intercalated graphite unstable?, *RSC Adv.*, 2017, **7**(58), 36550–36554.
 - 8 Z. Xu and J. Wang, Toward Emerging Sodium-Based Energy Storage Technologies: From Performance to Sustainability, *Adv. Energy Mater.*, 2022, **12**(29), 2201692.
 - 9 Y. Li, A. Vasileiadis, Q. Zhou, Y. Lu, Q. Meng and Y. Li, *et al.*, Origin of fast charging in hard carbon anodes, *Nat. Energy*, 2024, **9**(2), 134–142.
 - 10 S. You, Q. Zhang, J. Liu, Q. Deng, Z. Sun and D. Cao, *et al.*, Hard carbon with an opened pore structure for enhanced sodium storage performance, *Energy Environ. Sci.*, 2024, **17**(21), 8189–8197.
 - 11 J. Peng, H. Wang, X. Shi and H. J. Fan, Ultrahigh Plateau-Capacity Sodium Storage by Plugging Open Pores, *Adv. Mater.*, 2024, 2410326.
 - 12 E. O. Eren, E. Senokos, Z. Song, E. B. Yilmaz, I. Shekova and B. Badamdorj, *et al.*, Conformal carbon nitride thin film inter-active interphase heterojunction with sustainable carbon enhancing sodium storage performance, *J. Mater. Chem. A*, 2023, **11**(3), 1439–1446.
 - 13 Z. H. Tian, Y. Zhang, J. X. Zhu, Q. Y. Li, T. X. Liu and M. Antonietti, A Reanalysis of the Diverse Sodium Species in Carbon Anodes for Sodium Ion Batteries: A Thermodynamic View, *Adv. Energy Mater.*, 2021, **11**(47), 2102489.
 - 14 K. Gotoh, T. Ishikawa, S. Shimadzu, N. Yabuuchi, S. Komaba and K. Takeda, *et al.*, NMR study for electrochemically inserted Na in hard carbon electrode of sodium ion battery, *J. Power Sources*, 2013, **225**, 137–140.
 - 15 C. Bommier, T. W. Surta, M. Dolgos and X. Ji, New Mechanistic Insights on Na-Ion Storage in Nongraphitizable Carbon, *Nano Lett.*, 2015, **15**(9), 5888–5892.
 - 16 P. X. Bai, Y. W. He, X. X. Zou, X. X. Zhao, P. X. Xiong and Y. H. Xu, Elucidation of the Sodium-Storage Mechanism in Hard Carbons, *Adv. Energy Mater.*, 2018, **8**(15), 1703217.
 - 17 Y. Zeng, J. Yang, H. Yang, Y. Yang and J. Zhao, Bridging Microstructure and Sodium-Ion Storage Mechanism in Hard Carbon for Sodium Ion Batteries, *ACS Energy Lett.*, 2024, **9**(3), 1184–1191.
 - 18 D. A. Stevens and J. R. Dahn, The Mechanisms of Lithium and Sodium Insertion in Carbon Materials, *J. Electrochem. Soc.*, 2001, **148**(8), A803.
 - 19 Y. Cao, L. Xiao, M. L. Sushko, W. Wang, B. Schwenzer and J. Xiao, *et al.*, Sodium Ion Insertion in Hollow Carbon Nanowires for Battery Applications, *Nano Lett.*, 2012, **12**(7), 3783–3787.
 - 20 P. Bai, Y. He, X. Zou, X. Zhao, P. Xiong and Y. Xu, Elucidation of the Sodium-Storage Mechanism in Hard Carbons, *Adv. Energy Mater.*, 2018, **8**(15), 1703217.
 - 21 L. Kitsu Iglesias, E. N. Antonio, T. D. Martinez, L. Zhang, Z. Zhuo and S. J. Weigand, *et al.*, Revealing the Sodium Storage Mechanisms in Hard Carbon Pores, *Adv. Energy Mater.*, 2023, **13**(44), 2302171.
 - 22 D. Chen, W. Zhang, K. Luo, Y. Song, Y. Zhong and Y. Liu, *et al.*, Hard carbon for sodium storage: mechanism and optimization strategies toward commercialization, *Energy Environ. Sci.*, 2021, **14**(4), 2244–2262.
 - 23 E. Begüm Yılmaz, E. Oğuzhan Eren, T. Horner, Z. Song, Y. Sheidaei and I. Siewert, *et al.*, Reductive Carbon Materials: Tailoring Chemistry and Electronic Properties to Improve Sodium-Ion Batteries, *Angew. Chem., Int. Ed.*, 2025, **64**(13), e202422714.
 - 24 J. R. Rodriguez, S. B. Aguirre and V. G. Pol, Understanding sodium-ion battery anodes through operando spectroscopic techniques, *Electrochim. Acta*, 2019, **319**, 791–800.
 - 25 D. Saurel, A. Pendashteh, M. Jáuregui, M. Reynaud, M. Fehse, M. Galceran and M. Casas-Cabanas, Experimental Considerations for Operando Metal-Ion Battery Monitoring using X-ray Techniques, *Chem.:Methods*, 2021, **1**(6), 249–260.
 - 26 E. O. Eren, C. Esen, E. Scoppola, Z. Song, E. Senokos and H. Zschiesche, *et al.*, Microporous Sulfur–Carbon Materials with Extended Sodium Storage Window, *Adv. Sci.*, 2024, **11**(16), 2310196.
 - 27 D. A. Stevens and J. R. Dahn, An In Situ Small-Angle X-Ray Scattering Study of Sodium Insertion into a Nanoporous Carbon Anode Material within an Operating Electrochemical Cell, *J. Electrochem. Soc.*, 2000, **147**(12), 4428.
 - 28 Y. Morikawa, S.-I. Nishimura, R.-I. Hashimoto, M. Ohnuma and A. Yamada, Mechanism of Sodium Storage in Hard Carbon: An X-Ray Scattering Analysis, *Adv. Energy Mater.*, 2020, **10**(3), 1903176.
 - 29 J. S. Weaving, A. Lim, J. Millichamp, T. P. Neville, D. Ledwoch and E. Kendrick, *et al.*, Elucidating the Sodiation Mechanism in Hard Carbon by Operando Raman Spectroscopy, *ACS Appl. Energy Mater.*, 2020, **3**(8), 7474–7484.
 - 30 X. Feng, Y. Li, Y. Li, M. Liu, L. Zheng and Y. Gong, *et al.*, Unlocking the local structure of hard carbon to grasp sodium-ion diffusion behavior for advanced sodium-ion batteries, *Energy Environ. Sci.*, 2024, **17**(4), 1387–1396.
 - 31 X. Liu, N. Fechner, M. Antonietti, M. G. Willinger and R. Schlögl, Synthesis of novel 2-d carbon materials: sp² carbon nanoribbon packing to form well-defined nanosheets, *Mater. Horiz.*, 2016, **3**(3), 214–219.
 - 32 L. Qie, W. Chen, X. Xiong, C. Hu, F. Zou, P. Hu and Y. Huang, Sulfur-Doped Carbon with Enlarged Interlayer Distance as a High-Performance Anode Material for Sodium-Ion Batteries, *Adv. Sci.*, 2015, **2**(12), 1500195.
 - 33 J. Yang, X. Zhou, D. Wu, X. Zhao and Z. Zhou, S-Doped N-Rich Carbon Nanosheets with Expanded Interlayer Distance as Anode Materials for Sodium-Ion Batteries, *Adv. Mater.*, 2017, **29**(6), 1604108.
 - 34 A. C. Ferrari and J. Robertson, Interpretation of Raman spectra of disordered and amorphous carbon, *Phys. Rev. B:Condens. Matter Mater. Phys.*, 2000, **61**(20), 14095–14107.
 - 35 S. Roscher, R. Hoffmann and O. Ambacher, Determination of the graphene–graphite ratio of graphene powder by Raman 2D band symmetry analysis, *Anal. Methods*, 2019, **11**(9), 1224–1228.
 - 36 A. Sadezky, H. Muckenhuber, H. Grothe, R. Niessner and U. Pöschl, Raman microspectroscopy of soot and related



- carbonaceous materials: Spectral analysis and structural information, *Carbon*, 2005, **43**(8), 1731–1742.
- 37 A. Kaniyoor and S. Ramaprabhu, A Raman spectroscopic investigation of graphite oxide derived graphene, *AIP Adv.*, 2012, **2**(3), 032183.
- 38 K. Schutjajew, T. Tichter, J. Schneider, M. Antonietti, C. Roth and M. Oschatz, Insights into the sodiation mechanism of hard carbon-like materials from electrochemical impedance spectroscopy, *Phys. Chem. Chem. Phys.*, 2021, **23**(19), 11488–11500.
- 39 C. Plank, T. R  ther, L. Jahn, M. Schamel, J. P. Schmidt, F. Ciucci and M. A. Danzer, A review on the distribution of relaxation times analysis: A powerful tool for process identification of electrochemical systems, *J. Power Sources*, 2024, **594**, 233845.
- 40 J. Liu, J. Wang, C. Xu, H. Jiang, C. Li and L. Zhang, *et al.*, Advanced Energy Storage Devices: Basic Principles, Analytical Methods, and Rational Materials Design, *Adv. Sci.*, 2018, **5**(1), 1700322.
- 41 T. S. Mathis, N. Kurra, X. H. Wang, D. Pinto, P. Simon and Y. Gogotsi, Energy Storage Data Reporting in Perspective-Guidelines for Interpreting the Performance of Electrochemical Energy Storage Systems, *Adv. Energy Mater.*, 2019, **9**(39), 1902007.
- 42 Y. Li, Y.-S. Hu, M.-M. Titirici, L. Chen and X. Huang, Hard Carbon Microtubes Made from Renewable Cotton as High-Performance Anode Material for Sodium-Ion Batteries, *Adv. Energy Mater.*, 2016, **6**(18), 1600659.
- 43 K. Wang, Y. Jin, S. Sun, Y. Huang, J. Peng and J. Luo, *et al.*, Low-Cost and High-Performance Hard Carbon Anode Materials for Sodium-Ion Batteries, *ACS Omega*, 2017, **2**(4), 1687–1695.
- 44 C. Bommier, T. W. Surta, M. Dolgos and X. Ji, New Mechanistic Insights on Na-Ion Storage in Nongraphitizable Carbon, *Nano Lett.*, 2015, **15**(9), 5888–5892.
- 45 C. J. Jafta, A. Petzold, S. Risse, D. Clemens, D. Wallacher, G. Goerigk and M. Ballauff, Correlating pore size and shape to local disorder in microporous carbon: A combined small angle neutron and X-ray scattering study, *Carbon*, 2017, **123**, 440–447.
- 46 D. Saurel, J. Segalini, M. Jauregui, A. Pendashteh, B. Daffos, P. Simon and M. A. Casas-Cabanas, SAXS outlook on disordered carbonaceous materials for electrochemical energy storage, *Energy Storage Mater.*, 2019, **21**, 162–173.
- 47 Q. Li, X. Liu, Y. Tao, J. Huang, J. Zhang and C. Yang, *et al.*, Sieving carbons promise practical anodes with extensible low-potential plateaus for sodium batteries, *Natl. Sci. Rev.*, 2022, **9**(8), nwac084.
- 48 S. Huang, Z. Li, B. Wang, J. Zhang, Z. Peng and R. Qi, *et al.*, N-Doping and Defective Nanographitic Domain Coupled Hard Carbon Nanoshells for High Performance Lithium/Sodium Storage, *Adv. Funct. Mater.*, 2018, **28**(10), 1706294.
- 49 X. Chen, C. Liu, Y. Fang, X. Ai, F. Zhong, H. Yang and Y. Cao, Understanding of the sodium storage mechanism in hard carbon anodes, *Carbon Energy*, 2022, **4**(6), 1133–1150.
- 50 X. Yin, Z. Lu, J. Wang, X. Feng, S. Roy and X. Liu, *et al.*, Enabling Fast Na⁺ Transfer Kinetics in the Whole-Voltage-Region of Hard-Carbon Anodes for Ultrahigh-Rate Sodium Storage, *Adv. Mater.*, 2022, **34**(13), 2109282.
- 51 R. Ven  ncio, R. Vicentini, L. H. Costa, R. Te  filo, L. M. Da Silva and H. Zanin, In-situ electrochemical and operando Raman techniques to investigate the effect of porosity in different carbon electrodes in organic electrolyte supercapacitors, *J Energy Storage*, 2022, **50**, 104219.
- 52 C. Schmitt, A. Kube, N. Wagner and K. A. Friedrich, Understanding the Influence of Temperature on Phase Evolution during Lithium-Graphite (De-)Intercalation Processes: An Operando X-ray Diffraction Study, *ChemElectroChem*, 2022, **9**(2), e202101342.
- 53 D. Igarashi, R. Tatara, R. Fujimoto, T. Hosaka and S. Komaba, Electrochemical intercalation of rubidium into graphite, hard carbon, and soft carbon, *Chem. Sci.*, 2023, **14**(40), 11056–11066.
- 54 S. Qiu, L. Xiao, M. L. Sushko, K. S. Han, Y. Shao and M. Yan, *et al.*, Manipulating Adsorption-Insertion Mechanisms in Nanostructured Carbon Materials for High-Efficiency Sodium Ion Storage, *Adv. Energy Mater.*, 2017, **7**(17), 1700403.
- 55 B. Zhang, C. M. Ghimbeu, C. Laberty, C. Vix-Guterl and J.-M. Tarascon, Correlation Between Microstructure and Na Storage Behavior in Hard Carbon, *Adv. Energy Mater.*, 2016, **6**(1), 1501588.
- 56 X. Shi, H. Wang, Z. Xie, Z. Mao, T. Zhang and J. Jin, *et al.*, A Dual-Carbon Potassium-Ion Capacitor Enabled by Hollow Carbon Fibrous Electrodes with Reduced Graphitization, *Adv. Mater.*, 2024, **36**(36), 2406794.
- 57 F. Karcher, M. Uhl, T. Geng, T. Jacob and R. Schuster, Entropic Contributions to Sodium Solvation and Solvent Stabilization upon Electrochemical Sodium Deposition from Diglyme and Propylene Carbonate Electrolytes, *Angew. Chem.*, 2023, **135**(22), e202301253.
- 58 A. C. S. Jensen, H. Au, S. G  rtner, M.-M. Titirici and A. J. Drew, Solvation of NaPF₆ in Diglyme Solution for Battery Electrolytes, *Batteries Supercaps*, 2020, **3**(12), 1306–1310.

