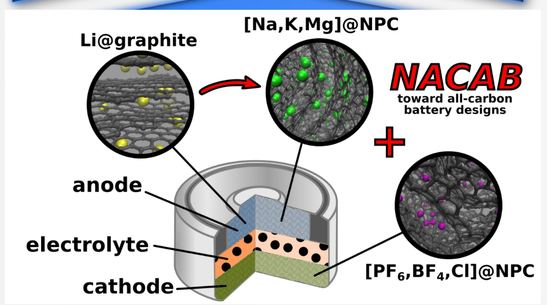
Summary

- Li ions are not sustainable.
- Sustainable intercalants such as Na to not migrate well into graphite
- Other forms of carbon may be better suited.
- We show how sustainable forms of carbon from nanocellulose can create good sodium batteries.
- We characterize different nanocellulose anodes and show that TCNF derived anodes perform best.
- We deduce atomic structure from simulations which match the experimental data by design with a novel atomistic theory and assess how well a-C intercalates Na vs graphite.
- With this new theory, we can deduce more experimentally-valid structures.

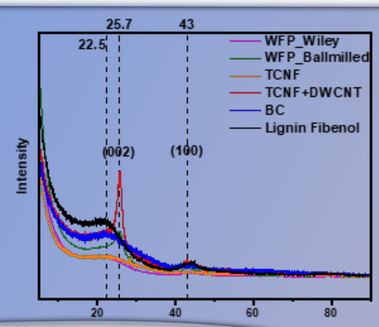


Synthesis

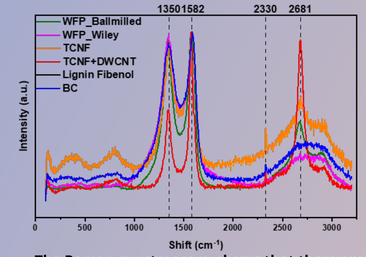
- Hard carbons were synthesized from Bacterial Nanocellulose (BC), Tempo-cellulose nanofiber (TCNF) and Whatman Filter Paper (WFP).
- Synthesis process:
1. Freeze drying
2. Pre-carbonization treatment at 300 °C for 2 hours in nitrogen.
3. Pyrolyzed at 1200 °C for 1 hour in nitrogen.

XRD

XRD patterns show the structural difference between the different nanocellulose electrodes. We see a greater amount of graphitic content apparent in the TCNF+DWCNT. The diffuse peaks of the rest suggest varying amounts of sp^2 content.



Raman



The Raman spectroscopy shows that there are large differences between the D and G peaks, which correspond to the amount of disorder/ sp3 like content and the amount of graphitic content respectively.

Atomistic Simulations: Creating Experimentally Viable Structures By Design

We fit structures to the experimental XRD data by using Molecular Augmented Dynamics with a Machine Learned Potential (GAP - Gaussian Approximation Potentials) to deduce the atomic structure of these materials.

$$\tilde{V} = \frac{\gamma}{2}\sum_i^M w_i^2 \left(h^i_{\text{pred}} - h^i_{\text{exp}}\right)^2$$

Experimental Potential.

$$\tilde{f}_k^{\alpha} = -\frac{\partial \tilde{V}}{\partial r_k^{\alpha}} = -\gamma \mathbf{w} \odot \frac{\partial \mathbf{h}_{\text{pred}}(\{\mathbf{r}\})}{\partial r_k^{\alpha}} \cdot \mathbf{w} \odot \left(\mathbf{h}_{\text{pred}}(\{\mathbf{r}\}) - \mathbf{h}_{\text{exp}}\right)$$

Experimental Forces.

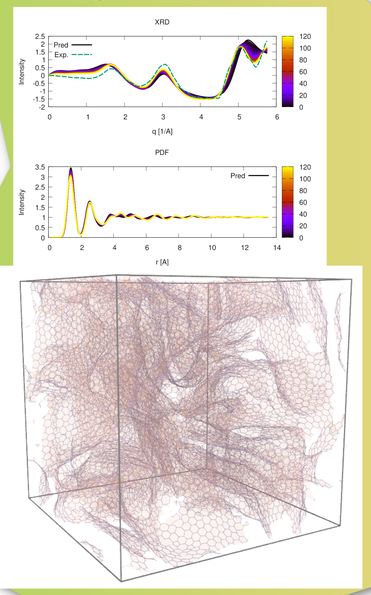
$$f_k^{\alpha,\,\text{tot}} = f_k^{\alpha} + \sum_i^M \tilde{f}_k^{\alpha,i}$$

Added to Machine Learned potential.

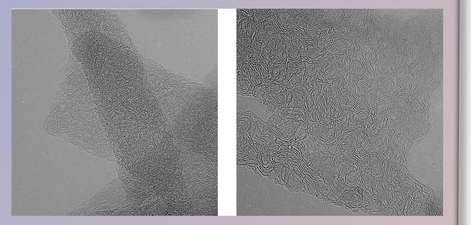
Experimentally-valid atomistic structure

Molecular Dynamics Anneal

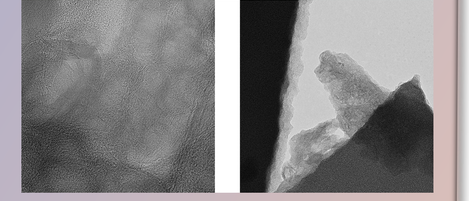
Fitting XRD structure



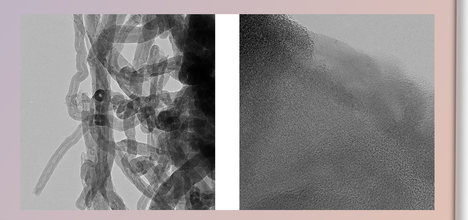
HRTEM BC



HRTEM TCNF



HRTEM TCNF/DWCNT



Nanocellulose-derived hard carbons for sustainable Na-ion anodes: an experimental and computational study

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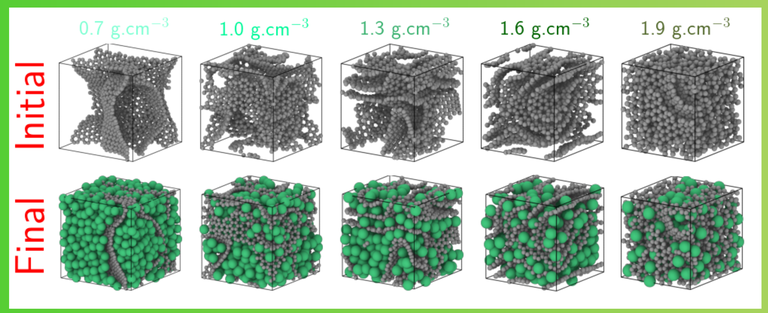
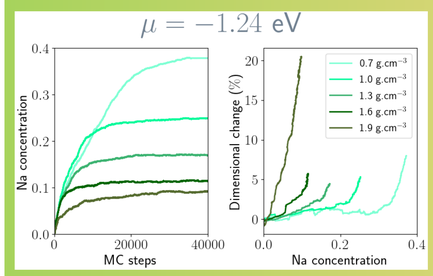
References

[1] Tigany Zarrouk, Rina Ibragimova, Albert P. Bartók, and Miguel A. Caro, "Experiment-Driven Atomistic Materials Modeling: A Case Study Combining X-Ray Photoelectron Spectroscopy and Machine Learning Potentials to Infer the Structure of Oxygen-Rich Amorphous Carbon," Journal of the American Chemical Society 146,14645–14659 (2024).

Intercalation of Na in a-C vs graphite.

Performing GCMC simulations on amorphous materials, we show the effect of increasing Na content on the dimensional change. f We show that there is a large increase in dimensional change with Na content in graphite compared to that of nanoporous carbon.



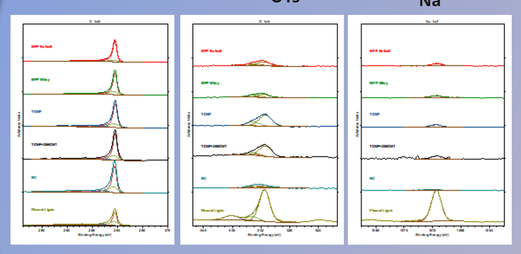


Conclusion

With this work, we show that Na can be used with sustainable carbon electrodes synthesized from nanocellulose. These electrodes are able to efficiently intercalate Na, as shown by the exemplary electrochemical performance.

With these new types of simulation, which match experiment explicitly, more atomistic structurure determination can be done. This type of simulation is able to be done with multiple types of experimental data, to remove the inherent structural degeneracies present in XRD, thereby improving our agreement with experiment, and further refining the structures generated.

XPS



XPS deconvolution of C1s shows differing proportions of O content is residual in the structures.

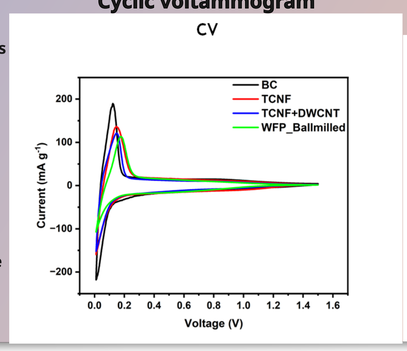
However, there are inherent accuracies with experimental deconvolution. Atomistic methods we have developed [1] to circumvent this problem, which is future work.

Electrochemical Performance

CV shows adsorption of Na+ in these electrodes through the wide diffuse peak, with the large primary peak showing the de/intercalation process.

Good cycling performance is shown by TCNF the most

Cyclic voltammogram



Cycling Performance