Core-Shell: Resolving the Dilemma of Hard Carbon Anodes by Sealing Nanoporous Particles with Semi-Permeable Coatings

Paul A. Appel[a], Carsten Prinz[b], Jian Liang Low[a], [c], Nahom Enkubahri Asres[b], Shu-Han Wu[a], Annica I. Freytag[d], Jonas Krug von Nidda[a], Nader de Sousa Amadeu[b] and Tim-Patrick Fellinger*[a]

BAM
Bundesanstalt für Materialforschung und -prüfung

Abstract: A core-shell strategy is introduced to overcome the dilemma of common non-graphitic hard carbon anodes.[1] Highly porous activated carbons are sealed by kinetically tuned gas-phase deposition of non-graphitic carbon to form a functional core-shell structure. Diethyl carbonate sorption analysis is introduced as a more suitable tool than N_2 or CO_2 sorption. The functional core-shell particles with much reduced diethyl carbonate uptake allow for high storage capacity and reduced first cycle losses. Delivering 400 ± 24 mAh g^{-1} with 82 ± 2 % first-cycle reversibility, it is shown that three-stage Na storage in designed core-shell anodes can compensate for the larger size of sodium compared to lithium stored in graphite anodes (372 mAh g^{-1}).

Core – Shell Carbons

Activated Carbons

- **Commercially available** – easy to produce
- Ideal core material for coating techniques – **highly microporous**
- However, **high irreversible capacities -** low reversible capacities

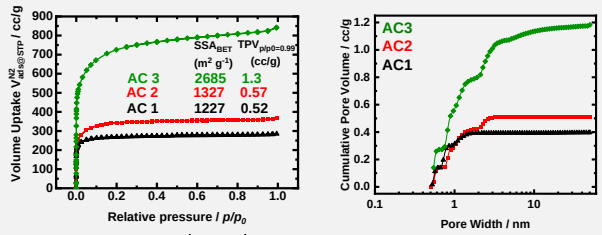


Figure 1: **Left:** *N_2 (77.4 K) adsorption–desorption isotherms as well as specific surface area (SSA) and total pore volume (TPV) calculated.* **Right:** *Cumulative pore volume based on QSDFT slit/cylindrical/spherical pores.*

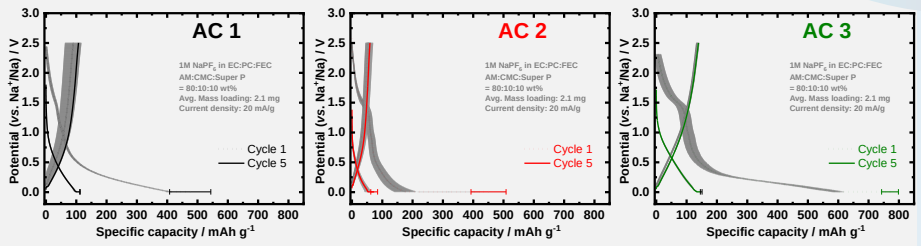
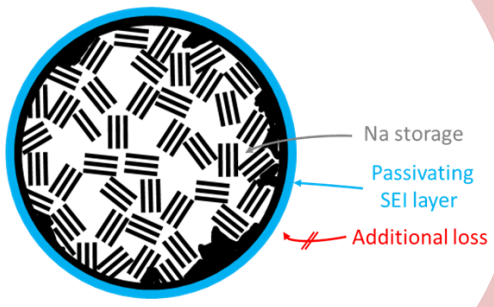


Figure 2: Charge/discharge half-cell voltage curves of highly porous activated carbon anodes (n=3)

Core-Shell Carbon (heterogeneous)
Electrolyte sieving / Na-ion penetrable



Carbon Anodes, functionally analogous to Graphite, with spacial separation of storage and passivation

Advanced Characterization

Electrolyte vapour sorption

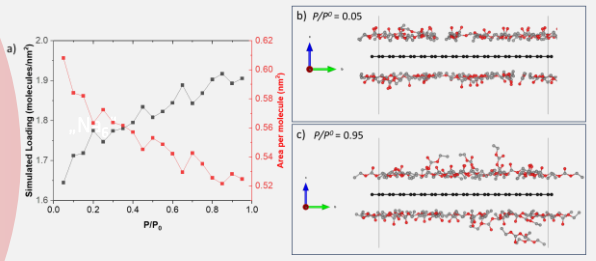


Figure 5: DFT simulations for DVS adsorption of DEC

- Surface area measurements with small probe molecules like N_2 and CO_2 are not reliable for hard carbons
- We tested dynamic vapor sorption (DVS) with diethyl carbonate (DEC), a representative carbonate electrolyte solvent molecule, as alternative technique
- Allows quantification of the liquid-solid interface

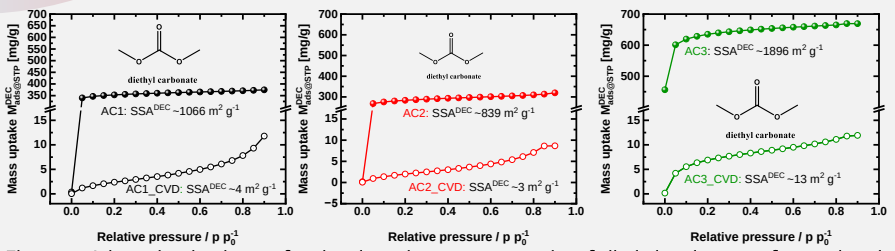


Figure 6: Adsorption isotherms for the electrolyte vapour uptake of diethyl carbonate of coated and uncoated activated carbons.

Coated Activated Carbons

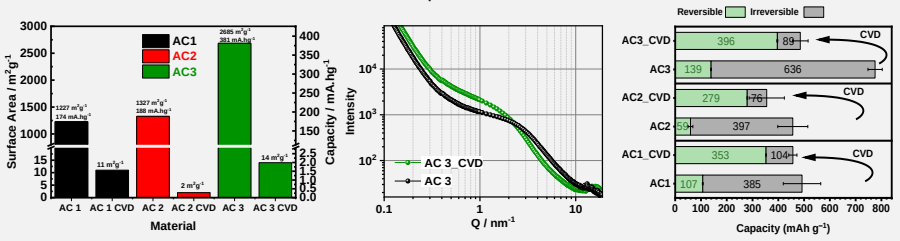


Figure 3: **Left:** *N_2 (77.4 K) SSA of activated carbons AC1, AC2 and AC3 before and after CVD coating.* **Middle:** *Small angle x-ray scattering (SAXS) pattern of AC3 and AC3_CVD* **Right:** *Reversible and irreversible capacity of uncoated and coated activated carbons (n =3).*

- **Reduction** in N_2 and CO_2 **SSA** and **pore volume**
- Transformation of **external** into **internal porosity**
- Significant retention of pore volume (SAXS)
- Coating seems to **prevent** excessive **solid electrolyte interphase (SEI)** formation
- Coating gives access to **large reversible Na-storage**

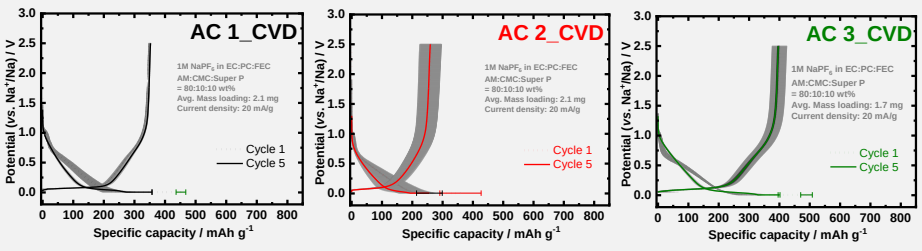


Figure 4, : Charge/discharge half-cell voltage curves of CVD coated highly porous core carbons (n=3).

- ✓ Successful **development of CVD method**
- ➢ Application to other core materials
- ➢ Created **internal porosity** can be used for **reversible Na-storage**

Ex-situ NMR

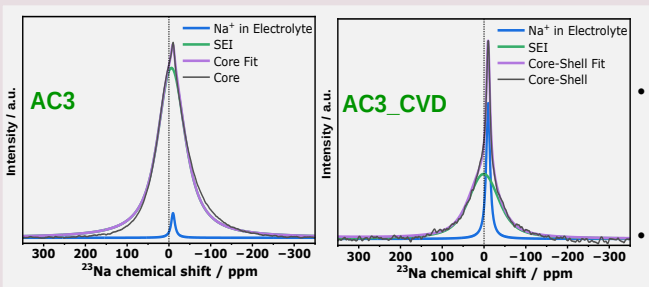


Figure 7 : Ex-situ ^{23}Na NMR spectroscopy of cycled AC3 (core carbon) and AC3_CVD (core-shell carbon) showing the characteristic SEI peak at -10 ppm.

- AC3 shows large and broad signal, composed of an SEI-related peak, with much higher intensity compared to the free electrolyte
- Signal for AC3_CVD remains sharp, pointing to much less significant formation of such species.

Operando NMR

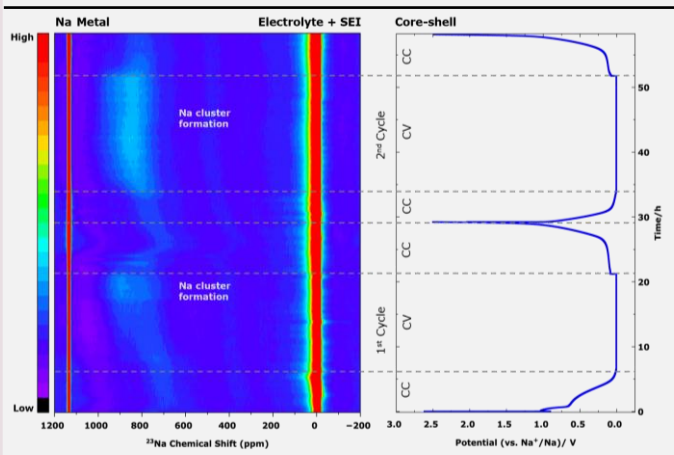


Figure 8: Operando ^{23}Na solid-state NMR spectra of an electrochemical half-cell comprising core–shell carbon, sodium metal, and $NaPF_6$ electrolyte.

- Probed the different Na-containing local environments - Diamagnetic sodium ions: the $NaPF_6$ electrolyte and Na^+ in the bulk electrode and SEI layer
- Clearly shows formation of clusters during low voltage plateau

- ✓ Successful **characterization of core-shell material**
- ➢ Shows that electrolyte exclusion enables superior performance
- ➢ **Internal porosity** can be used for **reversible Na-storage via clusters.**

Conclusion: Core–shell carbon materials enable competitive capacities for sodium ion battery anodes. These materials enable an understanding of the sodium storage mechanism and show that electrolyte exclusion is key in enabling high reversible capacities for porous carbons. The concept of core-shell carbons should ideally help to relate porosity to capacity values.

Sicherheit in Technik und Chemie

Source
[1] P. A. Appel, C. Prinz, J. L. Low, N. E. Asres, S.-H. Wu, A. I. Freytag, J. Krug von Nidda, N. de Sousa Amadeu and T.-P. Fellinger*, Angewandte Chemie, accepted, DOI: 10.1002/anie.202519457.

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