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Nanoconfinement as an electrolyte-state selector in hard carbon for sodium storage

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Table S1. Descriptor and proxy set for confined Na-electrolyte environments. The table summarizes practical descriptors used to place a hard-carbon/electrolyte system on the coordination-regime map. The descriptors are intended for transparent comparison, not for assigning universal thresholds.

Descriptor/proxy	What it captures	Preferred estimate	Practical alternative and main limitation
Confinement index (CI)	Geometric mismatch between the effective pore entrance and the solvated or associated Na^+ species.	Estimate from pore-mouth size or slit height divided by the electrolyte-specific solvated or associated Na^+ dimension[1].	Use gas sorption, SAXS, or microscopy combined with spectroscopy or MD-derived solvation size. The main limitation is that pore-mouth size and solvated-ion size are method-dependent.
Accessibility / closed-pore index (API)	Fraction of nominal microporosity that remains electrochemically accessible to Na^+ during formation and cycling.	Compare nominal pore volume with electrolyte uptake, pore-filling/recovery metrics, or *operando*/*ex situ* scattering evidence[2].	Electrochemical accessibility differs from gas-accessible porosity. Binder, density, wetting time, and slow infiltration can distort the estimate.
Connectivity and tortuosity transport index (TTI)	Through-plane ionic-pathway distortion and the ability to sustain the selected regime across electrode depth.	Use 3D imaging with image-based transport modeling, effective ionic conductivity, limiting-current tests, or validated thickness-dependent rate analysis[3].	Strongly affected by electrode thickness, density, binder distribution, calendering, and measurement direction.
Surface interaction strength proxy (SIS)	Ability of the surface to stabilize Na^+-solvent or Na^+-anion coordination motifs.	Use XPS-derived functional groups, heteroatom speciation, adsorption-energy trends, or calibrated spectroscopic shifts[4].	Bulk O/N content alone is insufficient. Surface chemistry changes during handling and cycling.
Solvation and ion-pair evidence	Local Na^+ coordination, including N_{solv} and SSIP/CIP/AGG tendencies.	Use Raman or NMR with explicit assignments, supported by MD/AIMD coordination analysis when possible[5].	Absolute fractions are sensitive to fitting models and force fields. Report definitions and uncertainty.
Desolvation and interphase proxy	Effective kinetic penalty for Na^+ reorganization and early interphase formation at confined entrances.	Use rate-temperature analysis, GITT/PITT, EIS/DRT with stable attribution, or PMF calculations[6].	These proxies can mix transport, charge-transfer, and interphase contributions. Controls are required.

Section S1. Practical estimation and validation of CI, API, and TTI

CI, API, and TTI are intentionally minimal descriptors. They do not provide complete mechanistic proof on their own. Their function is to make confinement, accessibility, and electrode-scale transport explicit when comparing hard-carbon/electrolyte systems.

CI compares the effective pore-mouth size with the size of the relevant solvated or associated Na^+ species. A lower CI indicates stronger geometric selection and a greater likelihood of solvation-shell reconstruction, partial desolvation, ion-pair redistribution, or exclusion of large associated species at the pore entrance. CI should be reported with the pore model, electrolyte composition, temperature, and the method used to estimate the relevant ion dimension. Pore-body size should not be substituted for pore-mouth size unless this assumption is justified[1]. The electrolyte-specific ion dimension should be supported by solvation evidence rather than assumed from bulk concentration alone[7].

API separates nominal porosity from electrochemically accessible porosity. This distinction is essential because gas-accessible micropores do not necessarily remain wetted, ionically connected, or open after formation. API can be constrained using electrolyte uptake, changes in pore-filling signatures, SAXS or related scattering, reversible pore-access indicators, and rate-temperature response. It should be reported with electrode density, thickness, binder content, wetting protocol, and cycling protocol[1]. Opened-pore hard-carbon data further illustrate that access can change during cycling[2].

TTI describes whether ionic supply through the electrode thickness can sustain the selected local regime at pore mouths. It is most useful for practical electrodes in which tortuosity, calendering, binder distribution, and thickness gradients strongly influence utilization. TTI can be estimated from 3D imaging, image-based transport modeling[3], effective ionic conductivity, limiting-current methods, or thickness-dependent rate and impedance analysis.

The descriptors should be validated through matched comparisons. A useful validation set includes: (i) the same hard carbon tested with electrolytes that shift SSIP/CIP/AGG tendencies[8]; (ii) different hard carbons with controlled pore-mouth size or accessibility tested in the same electrolyte[1]; and (iii) structural, solvation, interphase, and electrochemical measurements before and after cycling[2]. This logic helps distinguish electrolyte-state selection from intrinsic storage-site differences.

Section S2. Worked examples from published hard-carbon studies

This section illustrates how the descriptors can be applied retrospectively. The goal is not to define universal thresholds, but to show how published data can be converted into transparent comparisons.

A pore-mouth-controlled dataset reported carbon molecular sieves with different pore-mouth size classes tested in the same electrolyte[1]. For carbonate electrolytes, spectroscopy and simulations indicate that Na^+ maintains a relatively large multi-solvent coordination environment[7], so an effective solvated Na^+ diameter of 0.65-0.80 nm can be used as a conservative normalization range for qualitative comparison[9].

Using CI = pore-mouth size / effective solvated Na^+ diameter, CMS-800 with pore-mouth size of 0.35-0.50 nm gives CI approximately 0.44-0.77. CMS-1300 with pore-mouth size below 0.35 nm gives CI below approximately 0.44-0.54. These estimates coincide with different first-cycle outcomes in the same electrolyte, with CMS-800 showing lower ICE and CMS-1300 showing higher ICE. The interpretation is that smaller pore entrances impose stronger entry selection and favor a more pore-surviving interphase[1].

API can be estimated from pore-evolution metrics when confinement-resolved scattering is available. In the same dataset, an access-retention proxy can be approximated as API = Dafter / Dbefore from reported pore-diameter evolution. Activated carbon gives API approximately 0.42, CMS-800 gives API approximately 0.87, and CMS-1300 remains close to unity within the reported resolution. These values separate pore-filling-dominated behavior from pore-surviving behavior, while remaining approximate because pore accessibility is method-dependent[1].

A second example compares closed-pore hard carbon with opened-pore hard carbon. *Ex situ* SAXS indicates that the pore-related scattering feature recovers on charge for opened-pore hard carbon but not for the more closed architecture. This supports the idea that accessibility is dynamic and must be evaluated after cycling, not only in pristine powders[2].

Table S2. Retrospective descriptor examples from representative hard-carbon studies.

Case	Descriptor use	Main inference	Limitation
CMS pore-mouth series in the same carbonate electrolyte	CI estimated from pore-mouth size divided by effective solvated Na^+ diameter[1].	Smaller CI corresponds to stronger entry selection and higher likelihood of pore-surviving interphase.	Solvated-ion diameter and pore-mouth size are approximate and model-dependent.
CMS pore evolution after cycling	API approximated from pore-diameter retention after formation/cycling[1].	Low API indicates pore filling or blockage; high API indicates better pore survival.	API based on diameter retention does not fully capture pore-volume distribution or wetting.
Closed-pore vs opened-pore hard carbon	Qualitative API inferred from recovery of pore-related scattering features[2].	Opened pores show stronger reversible access to internal pore environments.	Dataset does not provide all inputs for strict CI/API calculation.
Practical thick-electrode comparison	TTI should be estimated from imaging, effective transport, or thickness-dependent electrochemistry[10].	Transport uniformity determines whether local regime selection is sustained across electrode depth.	TTI is highly sensitive to processing and electrode architecture.

Section S3. Interphase survival and validation priorities

In this article, interphase survival refers to the ability of the interphase to preserve ionic transport, mechanical continuity, and electrochemical access within confined geometries during repeated cycling. It is broader than initial SEI formation and more specific than SEI thickness alone. Confinement amplifies local current-density gradients, stress localization, and the effect of small deposits at pore throats[11]. A small absolute amount of interphase growth can therefore produce a large relative loss of access in narrow pores[12].

Organic-rich interphases associated with solvent-involved reduction are more likely to undergo continuous repair, electrolyte consumption, and impedance growth[13,14]. Inorganic-rich interphases can be more mechanically robust[15], but they can still fail if adhesion is poor or if growth is localized at a small number of entrances[12]. AGG-derived interphases may provide anion-derived passivation in some systems[16], but heterogeneous composition can also generate local mechanical mismatch under severe confinement[12].

Quantitative mechanical data remain limited for sodium hard-carbon systems. Across model Li systems, reported SEI moduli span from MPa-level values to multi-GPa values depending on chemistry, layering, and measurement protocol[15]. For sodium hard carbon, AFM studies report modulus values around 1-2 GPa for locally formed SEI regions[17], while electrolyte-dependent measurements have shown much higher modulus for ether-derived surface SEI than for ester-derived surface SEI[18]. Most of these measurements probe outer surfaces or local deposits rather than nanopore-confined interphases.

Future validation should therefore combine chemistry, mechanics, and transport rather than relying on any single descriptor. Minimum useful evidence includes: (i) solvation or ion-pairing evidence when a coordination-regime claim is made[5]; (ii) pore-accessibility evidence before and after cycling; (iii) interphase morphology or impedance evolution linked to pore survival[12]; and (iv) device-relevant testing conditions such as areal loading, electrode thickness, electrolyte amount, temperature, and rate protocol[19]. This evidence set supports the electrolyte-state selector framework without treating CI, API, or TTI as universal constants.

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