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Designing Organic Cathodes for Aqueous Zinc Batteries: Materials Chemistry of Carrier Selectivity, Mechanistic Validation, and Practical Benchmarking

Vipada Aupama[1], Wathanyu Kao-ian[2], Mohan Gopalakrishnan[2], Jun Huang[3], Jingwen Weng[4], Yuki Nagao[2,5], Soorathep Kheawhom[2,6,*]

[1]Department of Chemical Technology, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand

[2]Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand

[3]School of Chemical and Biomolecular Engineering, Sydney Nano Institute, The University of Sydney, Sydney, NSW 2037, Australia

[4]Department of Materials, Imperial College London, London SW7 2AZ, United Kingdom

[5]School of Materials Science, Japan Advanced Institute of Science and Technology, Nomi, Ishikawa 923-1292, Japan

[6]Center of Excellence on Advanced Materials for Energy Storage, Chulalongkorn University, Bangkok 10330, Thailand

*Corresponding author: Soorathep.k@chula.ac.th

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Table S1. Working terminology, scope boundaries, and carrier-identity tags used throughout this review.

Term	Working definition in this review	Mechanistic significance/ scope note
Organic cathode host	The redox-active organic phase that provides chemically defined storage sites in an aqueous zinc battery	The organic component must be mechanistically central to charge storage, not merely a conductive additive, binder, or passive scaffold
Redox site	The atom or functional group whose electronic state changes during charge/discharge	Redox site and coordination site may coincide, but they need not be identical
Coordination site	The atom or local donor environment that directly interacts with the incoming ionic carrier	Determines whether Zn^{2+} coordination is chemically plausible and how strongly the host can compete with proton-coupled pathways
Confinement environment	The local steric, electrostatic, and solvation landscape around the active site, including pore size, interlayer spacing, nearby donor groups, and hydrogen-bonding networks	Controls accessibility, partial desolvation, and the balance between Zn^{2+}- and H^+-coupled storage
Carrier identity	The dominant ionic species compensating electronic charge during cycling	Assigned here as Zn^{2+}-dominant**,** H^+-dominant**,** mixed**, or** unresolved
Partially desolvated Zn^{2+}	A Zn^{2+} species that retains part of its hydration shell while forming direct interactions with the host	More realistic than assuming complete dehydration before coordination in aqueous media
Zn^{2+}-dominant storage	Storage in which Zn^{2+} is the principal charge-compensating species under the stated conditions	Requires evidence that excludes a mainly proton-driven mechanism
H^+-dominant storage	Storage in which protonation or proton-coupled electron transfer provides most of the reversible charge compensation	Often associated with strong proton accessibility, hydrogen-bond networks, or local pH effects
Mixed storage	Storage in which both Zn^{2+} and H^+ contribute measurably, with relative contributions depending on electrolyte, rate, or potential window	Common in aqueous systems and should be treated as a mechanistic outcome rather than a classification failure

Term	Working definition in this review	Mechanistic significance/ scope note
Unresolved	Cases where the available evidence is insufficient to assign a dominant carrier confidently	Used when electrochemical or ex situ observations are suggestive but not definitive
Host-electrolyte-protocol combination	The specific combination of host chemistry, electrolyte composition, and testing conditions under which carrier identity is evaluated	Carrier assignment is not treated here as a fixed intrinsic property of the host alone
Fully organic host	A molecular, polymeric, or framework-based cathode in which the organic phase is the primary redox-active component	Included within the scope of this review
Hybrid / organometallic boundary case	A system containing both organic and inorganic or metal-centered components	Included only when the organic component remains mechanistically central to charge storage
Excluded systems	Systems in which the dominant redox chemistry occurs on an inorganic framework, and the organic component serves only as a conductive additive, structural support, binder, or otherwise passive modifier	Outside the scope of this review

Table S2. Operational descriptor framework for selective storage in organic aqueous zinc cathodes, including measurable or computable parameters, practical experimental proxies, representative host systems, and interpretive use.

Descriptor domain	**Operational parameter**	**Practical experimental/ computational proxy**	**Representative host examples**	**Interpretive use in this review**	**Current maturity**
Electronic	Zn^{2+} binding energy at reduced site; redox-potential shift upon coordination; charge localization / redistribution	DFT-computed binding energies; CV/DPV potential shifts; FTIR/Raman/XPS changes in carbonyl, imine, or radical environments	PBQS [1]; PTO derivatives [2]; HATN/HMHATN [3]	Estimates whether Zn^{2+} coordination is thermodynamically plausible relative to proton-coupled reduction; useful for comparing donor chemistry across host families	Readily computable / widely accessible
Geometric	Donor-donor spacing; bite angle; chelation topology; planarity / distortion upon reduction	DFT-optimized structures; crystallographic models; redox-state-dependent spectral changes consistent with structural rearrangement	TQD [4] (10.1039/D3TA01400B); TA-PTO-COF [5] (10.1039/D3SC07013A); BT-PTO [6] COF	Distinguishes whether a chemically plausible donor set is also structurally accessible for inner-sphere or cooperative Zn^{2+} coordination	Computable, but less consistently reported
Hydrogen-bonding / proton accessibility	Protonation energy; estimated pK_a shift of reduced site; H-bond connectivity / lifetime	D_2O isotope effects; buffer or pH dependence; in situ pH indicators; FTIR/Raman signatures of O-H or N-H formation; MD-derived H-bond statistics	HATN/HMHATN [3]; TQD [4]; PTO derivatives [2]	Evaluates how readily H^+ can compete with Zn^{2+} and whether mixed storage is chemically expected under aqueous conditions	Operationally accessible through proxies; quantitative treatment still uneven
Confinement	Pore aperture; pore size distribution; interlayer spacing; channel size;	Dry-state gas sorption/BET as an initial structural descriptor; XRD/SAXS; wet-state electrolyte	rPOP; BT-PTO COF [6]; TfDa-COF [8]	Assesses whether the host can stabilize partially desolvated Zn^{2+} through restricted	Readily measurable in porous/framework systems, but wet-state

Descriptor domain	Operational parameter	Practical experimental/ computational proxy	Representative host examples	Interpretive use in this review	Current maturity
	wet-state ion accessibility; electrolyte uptake/swelling behavior	uptake [7], swelling analysis, in situ SAXS/SANS, ion-accessible area estimates, and structural comparison of open versus confined analogues.		solvation and pre-organized donor environments	accessibility is less consistently quantified
Transport	Zn^{2+} diffusion coefficient; charge-transfer resistance; electronic conductivity; rate-dependent polarization	GITT/PITT; EIS; conductivity measurements; rate performance at matched loading / voltage window	PBQS [1]; rPOP [7]; PTEMPO-type cathode [9]	Tests whether the favored pathway remains observable at practical current density or becomes masked by faster proton or anion-coupled processes	Readily measurable, but often not compared under matched conditions
Descriptor-coupling / systems view	Co-variation of electronic, geometric, confinement, and transport terms	Cross-comparison of host series under matched electrolytes and loadings; qualitative high/moderate/low mapping across descriptor domains	PBQS [1]; HATN/HMHATN [3]; TA-PTO-COF [5]; PASP-TEMPO [10]	Prevents overinterpretation of any single descriptor and supports evidence-graded assignment of Zn^{2+}-dominant, H^+-dominant, mixed, or boundary-case behavior	Still developing; strongest when tied to controlled host series

Note on confinement descriptors. Dry-state porosity from gas sorption (e.g., N_2 BET) is a useful structural descriptor but is often a poor predictor of wet-state ion accessibility in aqueous organic cathodes. Electrolyte uptake, polymer swelling, pore wettability, and confinement-induced solvent restructuring can substantially modify the effective accessible volume during operation. Where confinement is invoked as a mechanistic advantage, dry-state BET should ideally be supplemented by wet-state probes such as electrolyte uptake measurements, in-situ SAXS or SANS, ion-permeable area estimates, or operando swelling characterization.

Note on DFT descriptors. Standard density functional theory (DFT) calculations of Zn^{2+} binding energies and related descriptors are sensitive to functional choice, treatment of aqueous solvation, and explicit modeling of confinement and electrolyte structure. GGA functionals routinely under- or over-estimate solvation contributions, and open-shell organic radicals require careful selection of functional and basis set. DFT-derived descriptors should therefore be read as plausibility indicators, ideally cross-validated against experimental observables (CV/DPV potentials, FTIR/Raman shifts, isotope effects), rather than as predictive carrier assignments. Continuum-plus-microsolvation treatments are preferred for aqueous descriptor work.

Table S3. Semi-quantitative ranges and representative values for descriptors in the operational framework. Ranges are indicative and aggregated from heterogeneous primary literature; they are intended for comparative interpretation, not absolute prediction. Where ranges are sparse, this is itself highlighted as a literature gap.

Descriptor domain	Operational parameter	Indicative range / typical reported magnitude	Comparative interpretation in this review
Electronic	DFT-computed Zn^{2+} binding energy at reduced site (cluster / fragment level)	Reported values typically span ~ -1 to -4 eV depending on coordination geometry, donor identity, and solvation model; values without explicit solvation often appear more negative.	Useful for ranking thermodynamic plausibility within a single computational protocol; absolute values are not directly comparable across studies with different functionals or solvation treatments.
Electronic	Redox-potential shift on Zn-salt addition (CV / DPV)	Tens to hundreds of mV in many carbonyl- and N-rich systems; smaller in p-type radical systems where Zn^{2+} is not the carrier.	Sensitive to electrolyte composition, IR drop, and reference-electrode choice; meaningful only when matched conditions are reported.
Geometric	Donor-donor spacing in proposed coordination motif	Typically ~ 2.5–4.5 Å in chelating carbonyl/imine pockets; broader in COFs/MOFs depending on linker.	Comparable to Zn-O / Zn-N distances in molecular complexes (~ 2.0–2.2 Å); donor spacing close to twice this range supports cooperative coordination.
Hydrogen bonding / proton accessibility	Estimated pK$_a$ shift on reduction; D$_2$O isotope effect on capacity / kinetics	ESI-derived pK$_a$ shifts of 1–3 units are commonly inferred for reduced quinone- or imine-type sites; D$_2$O isotope effects on rate are typically 1.5–3× when H$^+$ transfer is rate-relevant.	Strongly suggestive of H$^+$ coupling when both indicators are aligned; absence of isotope effect is informative but does not exclude minor H$^+$ contributions.
Confinement	Pore aperture / interlayer spacing (BET, SAXS, XRD)	Pore apertures of ~ 1–3 nm in many COF/POP systems; layer spacings of ~ 0.3–1 nm in stacked frameworks.	Comparable to the size of solvated and partially desolvated Zn^{2+} species (~ 0.3–0.6 nm); confinement claims should be paired with wet-state assessment (see BET note).
Transport	Apparent Zn^{2+} chemical diffusion coefficient (GITT/PITT)	Reported values range over several orders of magnitude (~ 10^{-10}-10^{-8} cm^2 s^{-1}) depending on host architecture and protocol.	Cross-study comparisons are limited by differing assumptions in GITT analysis; matched-protocol values are

Descriptor domain	Operational parameter	Indicative range / typical reported magnitude	Comparative interpretation in this review
			required for reliable benchmarking.
Coupling / systems view	Co-variation of descriptor scores under matched conditions	Quantitative coupling data sparse; most reports provide only qualitative coupling.	Highlighted as a research gap; controlled host series with matched electrolyte are needed.

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