

Photopolymer-Derived Supercapacitor Architectures: Porosity, Conductivity, Electrolyte Wetting and Cycle Life

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Abstract

Photopolymerization can define three-dimensional supercapacitor electrodes at high geometric resolution, but the printed resin rarely represents the final electrochemical state. Conductive polymers may be embedded in the resin, printed scaffolds may be metallized or coated, and polymer architectures may be pyrolyzed into carbon before pseudocapacitive phases are added. This review treats architecture, conductivity, electrolyte wetting and cycle life as coupled but non-interchangeable qualification axes. It distinguishes designed macroporosity from electrochemically accessible surface, separates electronic resistance from ionic transport, and requires capacitance claims to retain their mass, area or volume normalization basis. A non-compensatory framework is proposed in which high initial capacitance cannot offset poor wetting, high series resistance, unstable post-processing, or rapid capacity fade.

Keywords: supercapacitors; stereolithography; vat photopolymerization; porous electrodes; pyrolytic carbon; PEDOT; electrolyte wetting; cycle life; additive manufacturing

1. Significance and scope

Stereolithography and related photopolymerization routes have produced supercapacitor structures through several mechanisms: printed lattices subsequently plated and coated with graphene, stereolithography-derived pyrolytic carbon decorated with Mn₃O₄, and directly printed PEDOT-containing resin combined with a polymer gel electrolyte [1-3]. These routes share geometric control but not material state. ER-266 owns supercapacitor-specific architecture and qualification. ER-264 retains general electrochemical-electrode principles, while ER-265 retains battery-component integration.

1.1 Corpus boundary

Published incumbents retained as corpus boundaries are ER-07 for electrically functional photopolymer resins and ER-157 for conductivity, percolation, interfaces and anisotropy in functional nano/micron materials. ER-261 retains generic printed conductors, ER-264 retains general electrochemical-electrode qualification, and ER-265 retains battery-specific components and cell integration. These forward identifiers define scope only and carry no evidentiary authority for ER-266.

2. Designed porosity versus electrochemically accessible area

A lattice with high geometric porosity does not necessarily provide high accessible surface area. Macropores improve electrolyte penetration and shorten transport paths, while meso- and microporous features contribute much of the interfacial area for electric-double-layer storage. Coatings can narrow channels, pyrolysis can shrink struts, and wetting can exclude nominally open volume. Therefore report the designed geometry, the post-processed geometry and an electrochemically relevant accessibility measure separately. The successful hierarchical lattices reported by Xue and co-workers illustrate the value of combining printed cellular structure with additional porous graphene architecture [1].

3. Conductivity and current distribution

A supercapacitor electrode must move electrons through the entire 3D skeleton while ions move through the electrolyte-filled pore network. Those pathways are coupled by geometry but are not equivalent. Stereolithography-derived pyrolytic carbon can provide a continuous current-collecting scaffold, while Mn₃O₄ or other redox-active phases add pseudocapacitance [2]. PEDOT-containing photocurable systems offer another route in which conductivity is introduced within the printed resin state [3]. Bulk conductivity should not substitute for through-architecture resistance, contact resistance or equivalent series resistance measured in the assembled device.

4. Photopolymer fate and post-processing

The photopolymer may remain as part of the final electrode, serve as a sacrificial scaffold, or transform into carbon. Each pathway changes dimensions, pore size, conductivity and surface chemistry. Pyrolysis can create useful conductivity but also substantial shrinkage and mass loss; metallization or oxide deposition can change surface area and block constrictions. Qualification should therefore include before/after geometry, mass yield, dimensional change and the identity of the final load-bearing and current-carrying phase. Printed dimensions are not final electrode dimensions unless verified after all conversion steps.

5. Electrolyte wetting and ionic access

Electrolyte wetting determines whether nominal surface area participates in charge storage. Contact angle alone is insufficient for a thick 3D network because infiltration also depends on pore-throat size, trapped gas, viscosity, surface chemistry and time. A robust protocol records electrolyte composition, vacuum or pressure assistance if used, soak time and the electrochemical stabilization period. Poor wetting can appear as low capacitance, frequency dispersion or elevated resistance and may improve transiently during early cycles, so the initial state should not be conflated with the stabilized state.

6. Capacitance normalization and comparability

Specific, areal and volumetric capacitances answer different engineering questions. The mass denominator may include only active material, the complete electrode including carbon/current collector, or the whole device. Rezaei and co-workers explicitly reported the full electrode mass basis for their hybrid architecture [2], illustrating why denominator disclosure matters. Every capacitance, energy-density and power-density claim should state its normalization basis, voltage window, discharge method and whether values derive from a three-electrode or two-electrode configuration.

7. Cycling, rate capability and retention

A high capacitance at low current does not establish power performance or durability. Qualification should combine rate response, equivalent series resistance or impedance, Coulombic efficiency where meaningful, and cycle retention under a declared voltage window and temperature. Mechanical integrity also matters because a porous 3D scaffold can crack or delaminate while still retaining some short-term electrochemical response. Cycle-life claims should report the initial conditioning protocol and the absolute cycle count, not only percentage retention.

8. Device architecture and gel electrolytes

The PEDOT-based printed supercapacitor reported by Bertana and co-workers integrated a printed conductive resin with a polymer gel electrolyte [3]. Such quasi-solid systems add interfaces among electrode, gel and current collector that can dominate resistance and mechanical stability. Device-level qualification should therefore record gel composition, cure or crosslink state, assembly pressure, separator role if any, encapsulation and water or solvent loss where relevant. An electrode that performs well in liquid electrolyte cannot automatically be transferred to a gel device.

Gate	Required evidence	Blocking failure
G1 Final architecture	Post-processed dimensions, porosity and surface state	CAD geometry mistaken for electrode state
G2 Electronic path	Distributed conductivity/contact resistance or ESR	Charge cannot reach full architecture
G3 Ionic access	Declared electrolyte, wetting/infiltration and stabilization	Nominal area not electrochemically accessible
G4 Normalization	Mass/area/volume basis and two- vs three-electrode configuration	Performance cannot be compared
G5 Rate/cycle	Rate response, impedance/ESR and explicit cycle retention	Initial capacitance mistaken for durability
G6 Mechanical state	Cracking, delamination, shrinkage and interface integrity bounded	Electrochemical result detached from structural survival

9. Minimum reporting set

Report resin or precursor chemistry, printer and wavelength, layer thickness and orientation, post-cure, metallization/coating or pyrolysis schedule, post-process dimensions and mass, porosity or density, conductive phase, active phase loading, current collector, electrolyte and gel composition, wetting/soak protocol, electrode configuration, voltage window, current density or scan rate, capacitance calculation, normalization denominator, ESR or impedance method, rate sequence, conditioning cycles, final cycle count and retention, plus post-test visual or structural observations.

10. Knowledge boundary

The literature supports multiple viable stereolithography-enabled supercapacitor routes, but their metrics are not interchangeable because materials, normalization, electrode configurations and post-processing differ [1-5]. The review literature likewise emphasizes that stereolithography-derived electrodes span resin-based, carbon-based, ceramic and hybrid classes [4]. No universal porosity, conductivity, ESR or cycle-life threshold can therefore be inferred.

11. Conclusions

Photopolymer-derived supercapacitors should be qualified as coupled electronic, ionic and structural networks. Designed porosity has value only when electrolyte reaches it; conductivity has value only when the complete architecture carries current; capacitance has meaning only with a declared normalization basis; and initial performance has value only when the state remains stable under cycling. The final electrode state, not the uncured resin or CAD lattice, is the qualification object, and the weakest transport, structural or durability gate controls acceptance.

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