

Electrochemically Gated Polymerisation for Additive Manufacturing: Redox Control, Electrode Geometry and Spatial Selectivity

Assessing electric-potential control as a polymerisation gate while separating electrochemical synthesis from electrode-confined deposition

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Abstract

Electrochemical control can generate, activate or deactivate reactive species with temporal precision and can confine reaction near electrodes. For additive manufacturing the key question is whether the electric field or electrode reaction defines polymerisation volume reproducibly, rather than merely depositing a conducting polymer on a surface. This review combines electrochemically controlled polymerisation with emerging electrochemical additive manufacturing to define redox-state control, electrode geometry, transport and spatial selectivity.

Keywords: electrochemical polymerisation; additive manufacturing; redox gating; electrode geometry; spatial selectivity; electropolymerisation

1. Significance and scope

Electrochemically gated polymerisation is significant because electrical potential can localise redox chemistry independently of optical penetration, but only within the transport and field constraints imposed by electrodes and electrolyte. Qualification must connect applied electrical conditions to catalyst or monomer redox state, spatial selectivity and resulting conversion. Proprietary formulations and machine-specific tuning rules are outside scope.

1.1 Corpus boundary

ER-310 owns electrochemical triggering or gating of polymerisation as a spatial manufacturing control, including electrode geometry and redox state. It excludes electroplating of metals and post-print electrochemical switching of already formed devices. ER-306 owns photoredox chemistry and ER-309 owns mechanochemical activation and repair; ER-310 is limited to polymerisation gated by electrode potential, electrode geometry and electrochemical transport.

2. Mechanistic basis

Applied potential or current changes catalyst oxidation state, chain-end activity or monomer oxidation state. In electropolymerisation, reaction may be confined to the electrode/electrolyte interface; in mediated systems the activated species can diffuse away from the electrode. Spatial resolution is therefore set jointly by electron-transfer kinetics and mass transport [1].

3. State variables and process control

Potential, current density, electrode spacing, electrolyte composition, mediator concentration and diffusion length determine the active reaction volume. Turning current off is not proof of immediate stop if reactive intermediates persist. Light/electrochemical hybrid systems require separate controls for each stimulus. [1,2]

4. Principal failure modes

Loss of spatial selectivity can arise from mediator diffusion, ohmic drop, gas evolution or continued polymerisation after electrolysis. Electrode passivation changes local current distribution, while deposited polymer can modify the field and mass transport during the build. [2]

5. Measurement architecture

Qualification requires electrochemical traces, spatial mapping of deposited or polymerised volume, current efficiency or conversion, electrode geometry and repeatability across build height. A reaction-on/reaction-off experiment should measure residual growth after the gate is removed. [1,2]

6. Evidence hierarchy and transfer

Electrochemically controlled chain-growth polymerisation demonstrates reversible redox gating, while electrochemical additive-manufacturing studies show spatially confined electropolymer deposition. Redox-active polymers processed by DLP illustrate complementary integration of photoprinting and electrochemistry [1-3].

7. Qualification architecture

An electrochemically gated qualification package should retain electrode geometry, potential or current history, electrolyte state, redox-active species identity, spatial conversion map and controls at open circuit or non-productive potential. Current efficiency and diffusion length should be considered where they control the active zone. Transfer is justified only when the electrical field, mass transport and conversion pattern remain equivalent at the new scale.

8. Interpretation and decision logic

Decision logic should distinguish electrochemical gating from transport-driven loss of localisation. Spatial selectivity is supported when current or potential history, electrode geometry and the polymerised volume remain reproducibly coupled while mediator diffusion and parasitic electrochemistry are independently bounded.

Table 1. Qualification matrix for electrochemically gated polymerisation for additive manufacturing.

State variable	Minimum evidence	Qualification purpose
Electrical gate	Potential/current history	Defines activation
Electrode geometry	Spacing/shape	Defines spatial field
Transport state	Mediator/electrolyte diffusion	Bounds reaction spread
Polymerised volume	3D morphology/conversion	Measures spatial selectivity

9. Diagnostic interpretation matrix

The diagnostic matrix should distinguish insufficient overpotential, transport-limited propagation, parasitic electrochemistry, uncontrolled bulk reaction and genuinely gated polymerisation. Spatial selectivity should be interpreted against electrode geometry and species diffusion, not electrical input alone.

Table 2. Diagnostic interpretation matrix for electrochemically gated polymerisation.

Observed deviation	Competing mechanism	Discriminating check
Growth after current off	Persistent intermediate	Off-time growth test
Broad deposition	Mediator diffusion	Concentration/spacing study
Nonuniform build	Ohmic drop/passivation	Potential/current map
Gas/voids	Side electrochemistry	Gas/current-efficiency check

10. Limitations and evidence gaps

The literature spans fundamentally different modes: solution polymerisation under electrochemical control, meniscus-guided electropolymerisation and post-print electroactive materials. Their spatial physics cannot be merged into one performance claim. The review therefore focuses on the conditions required for a true manufacturing gate.

11. Conclusions

Electrochemically gated additive manufacturing is credible when the applied electrical state defines polymerisation onset, stop and location with quantified transport limits. Electrode geometry and mediator diffusion are part of the process definition, not secondary hardware details.

References

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Competing interests

The author is Founder, CEO and CTO of 3Dresyns by Resyner Technologies S.L. No comparative product recommendation is made.

Data availability

No new experimental dataset was generated for this review.