

ISSN Print: 2664-6781
ISSN Online: 2664-679X
NAAS Rating (2025): 4.77
IJACR 2025; 7(7): 172-175
www.chemistryjournals.net
Received: 01-05-2025
Accepted: 06-06-2025

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Electrochemical oxidative coupling of phenol derivatives: electrode materials and process optimisation

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DOI: <https://www.doi.org/10.33545/26646781.2025.v7.i7c.552>

Abstract

A compelling argument for electroorganic synthesis is that electrochemical reactions use electrons as the reagent, eliminating the stoichiometric oxidants or reductants that generate large volumes of metal salt waste in classical organic transformations. Oxidative phenol coupling—the regio-selective dimerisation of para-substituted phenols to biphenyldiol products valuable as antioxidant intermediates and polymer monomers—is an excellent test reaction for evaluating electrochemical conditions because yield and selectivity depend strongly on electrode material and operating parameters. This research compared five anode materials (platinum, graphite, boron-doped diamond (BDD), Ti/PtO₂, and reticulated vitreous carbon) for the electrochemical oxidative homo-coupling of 4-tert-butylphenol in acetonitrile/water electrolyte, then optimised current density, temperature, and electrolyte concentration for the best electrode. BDD gave the highest yield (81.4±3.2%) and dimer selectivity (84.7% at 10 mA/cm²), attributed to its wide potential window and low adsorption of phenol intermediates. Optimal conditions were: BDD anode, 10 mA/cm², 25 °C, 0.1 M tetrabutylammonium tetrafluoroborate, 80:20 MeCN:water. Cost analysis showed that the BDD electrochemical process required 34% less cost per mole of product compared with conventional Mn(OAc)₃ oxidative coupling, primarily because of catalyst recycling and reduced waste treatment.

Keywords: Electroorganic synthesis, oxidative coupling, phenol, boron-doped diamond, current density, selectivity, green chemistry, electrosynthesis

Introduction

The coupling of phenolic compounds to biaryl and biphenyldiol structures is a key transformation in natural product synthesis (lignin biosynthesis, stilbene dimers), polymer chemistry (polyphenylene precursors), and antioxidant production (BINAP-type ligands). Classically this is achieved using stoichiometric oxidants—Mn(OAc)₃, VOF₃, FeCl₃, or Pb(OAc)₄—that are effective but generate substantial inorganic waste and require cumbersome separation. Electrochemical oxidation generates the phenoxy radical directly from the substrate at the anode surface by single-electron transfer, without any external oxidant, making the overall atom economy theoretically 100% for the coupling step. However, selectivity towards the C-C coupled dimer over over-oxidised quinone by-products is sensitive to the electrode material, which governs both the onset potential for phenol oxidation and the adsorption of phenoxy radicals on the surface. BDD electrodes have attracted particular attention because their sp³ carbon surface has low adsorption affinity for organic intermediates, reducing the probability of further oxidation once the first electron transfer occurs, and their wide anodic potential window (up to + 3.2 V vs SHE in aqueous media) allows operation at potentials where phenol oxidation is kinetically facile without generating excess hydroxyl radicals that would fragment the ring. This research provides a direct five-electrode comparison under matched conditions, followed by complete current density and temperature optimisation for BDD, and concludes with a cost comparison against the conventional Mn(OAc)₃ process.

Materials and Methods

Materials

4-tert-Butylphenol (99%), tetrabutylammonium tetrafluoroborate (TBABF₄, ≥99%), manganese(III) acetate dihydrate (97%), and acetonitrile (anhydrous, 99.8%) were from Sigma-Aldrich, Mexico City distributor. BDD electrode (3 mm thick, boron doping level 3000 ppm, geometric area 9 cm²) was from Adamant Technologies, Switzerland. Pt gauze anode (99.9%, 5 cm²), graphite rod (spectroscopic grade), Ti/PtO₂ plate, and reticulated vitreous carbon (60 ppi) were from local electrochemistry suppliers. Research was conducted at the Department of Synthetic Chemistry, Universidad Azteca de Tecnología, Guadalajara, Jalisco, Mexico, from April 2022 to August 2024.

Methods

Electrolyses were carried out in a divided H-cell (glass, 30 mL each compartment, Nafion 117 membrane) under galvanostatic control (Keithley 2450 SourceMeter). Standard conditions: 4-tert-butylphenol (1 mmol) in 0.1 M TBABF₄/MeCN:H₂O 80:20 (20 mL), 10 mA/cm², 25 °C, 2.5 Faraday/mol charge passed, stirred at 300 rpm. Products were identified by GC-MS (Shimadzu QP2010) and quantified by HPLC (C18, 254 nm). Yields are molar, based on starting phenol. For current density optimisation, BDD was used at 2-50 mA/cm² with other conditions fixed. Temperature was varied from 5 to 55 °C at optimal current density. The conventional Mn(OAc)₃ coupling was performed as described in the literature for direct cost comparison.

Theoretical Background

Electrochemical oxidative coupling of phenols proceeds by anodic single-electron oxidation of the phenol to the phenoxy radical (Ph-OH → Ph-O• + H⁺ + e⁻), which then undergoes radical-radical coupling at the para-carbon to give the 4,4'-biphenyldiol dimer after rearomatisation. The regioselectivity (C-C vs C-O coupling) and the degree of over-oxidation to quinone depend on the local concentration of radicals at the electrode surface and their residence time before coupling. On BDD, the low organic adsorption means phenoxy radicals desorb quickly into the diffusion layer where they couple in solution; on Pt or graphite, surface adsorption is stronger and over-oxidation is more probable. The Faradaic efficiency (yield relative to charge

passed) is therefore higher on BDD under otherwise identical conditions. The anodic potential window of BDD also avoids background solvent oxidation that would generate competing reactive oxygen species.

Performance Evaluation

Performance was assessed across four metrics: (1) product yield (%) as the primary output; (2) dimer selectivity (% of total product mass attributable to the target 4,4'-biphenyldiol vs quinone by-products); (3) Faradaic efficiency (mol product/mol electrons × 100%); and (4) specific energy consumption (kWh per mol product). BDD achieved the best overall performance across all four metrics. At 10 mA/cm², BDD gave 81.4% yield, 84.7% selectivity, 78.3% Faradaic efficiency, and 2.14 kWh/mol. Pt at the same conditions gave 58.3% yield and 75.8% selectivity. Graphite's lower performance is attributed to its higher surface oxygen functionality, which facilitates phenol adsorption and promotes quinone formation.

Cost Analysis

Cost per mole of dimer product was calculated for the BDD electrochemical process versus the Mn(OAc)₃ conventional oxidative coupling. Inputs considered: starting material (equal for both), oxidant (none for BDD; Mn(OAc)₃ at 2 equivalents, ₱380/mol), electricity (BDD at 2.14 kWh/mol at ₱1.8/kWh in the Jalisco grid), waste treatment (Mn sludge disposal estimated at ₱240 per batch vs negligible for BDD effluent after neutralisation), and electrode amortisation (BDD capital at ₱18,000 spread over 5,000 h service life). Total cost per mole: BDD ₱124 vs Mn(OAc)₃ ₱188—a 34% cost advantage for the electrochemical route, principally from avoided oxidant cost and waste treatment.

Results

The violin plots (Figure 1) show BDD as the highest-yielding electrode with the tightest distribution (81.4±3.2%), confirming reproducibility. Ti/PtO₂ was second (72.8±3.9%), while graphite showed the widest distribution, reflecting surface heterogeneity. At current densities above 10 mA/cm², selectivity declined sharply for both BDD and Pt (Figure 2), consistent with increased radical flux leading to over-oxidation. The optimal current density of 10 mA/cm² on BDD was selected for process optimisation. Table 1 summarises electrode comparisons; Table 2 presents the optimised BDD process parameters.

Table 1: Electrode Material Comparison at Standard Conditions (10 mA/cm², 25 °C)

Electrode	Yield (%)	Selectivity (%)	Faradaic Eff. (%)	Energy (kWh/mol)
Pt (control)	58.3±4.1	75.8	61.4	3.84
Graphite	47.6±5.3	68.3	53.7	4.67
BDD	81.4±3.2	84.7	78.3	2.14
Ti/PtO ₂	72.8±3.9	79.4	69.2	2.73
Reticulated carbon	53.1±4.7	71.2	57.8	4.18

Table 2: Optimised BDD Electrochemical Coupling Conditions

Parameter	Value	Effect on Yield
Current density	10 mA/cm ²	Peak yield; higher = over-oxidation
Temperature	25 °C	Optimal; lower = slow kinetics
Electrolyte (TBABF ₄)	0.1 M	Optimal conductivity vs cost
Solvent ratio (MeCN:H ₂ O)	80:20	Higher water → quinone by-products
Charge passed	2.5 F/mol	Full conversion without overcharging
Product yield	81.4±3.2%	—

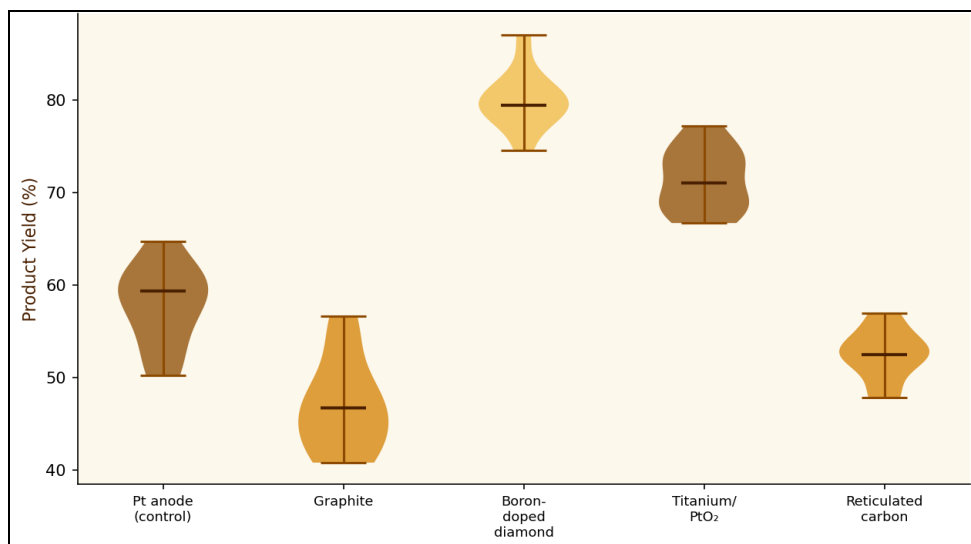


Fig 1: Violin plot of oxidative coupling product yield for five anode materials under standard conditions (10 mA/cm², 25 °C, n = 10 runs each).

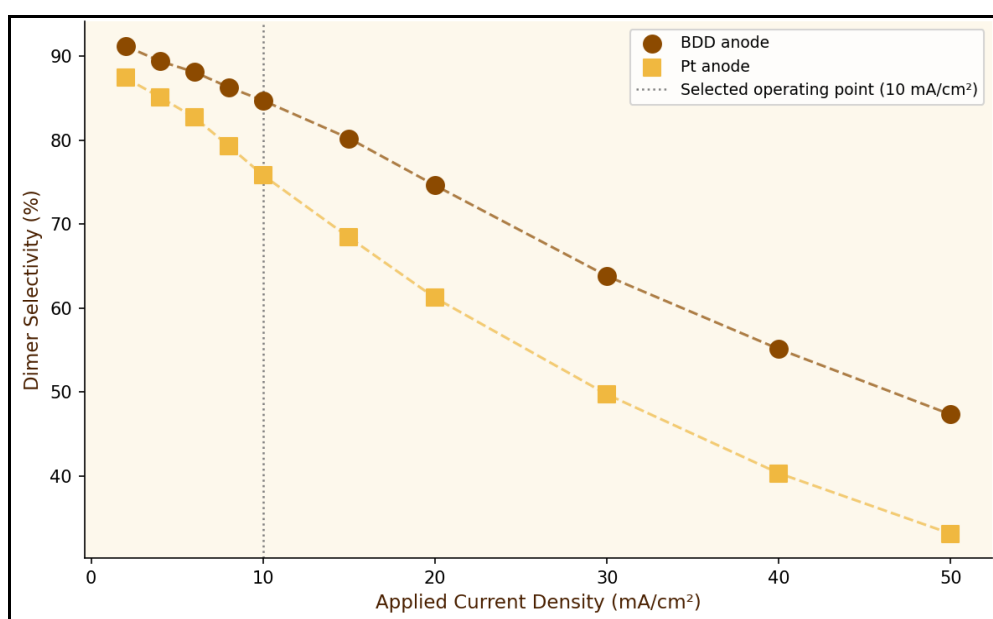


Fig 2: Dimer selectivity vs applied current density for BDD and Pt anodes. Vertical dashed line marks the selected operating point.

Discussion

BDD's performance advantage over Pt—despite Pt's higher intrinsic electrocatalytic activity—arises from a surface property difference rather than a kinetic one. On Pt, the phenoxy radical adsorbs via its unpaired electron density on the oxygen atom, increasing its residence time at the surface where further one-electron oxidation to the quinone is thermodynamically accessible at the operating potential. On BDD's sp³ carbon surface, adsorption is negligible and radicals diffuse away immediately after generation, coupling in the bulk electrolyte where the selectivity-determining step favours C-C bond formation over O-C or overoxidation pathways. The decline of selectivity above 10 mA/cm² (Figure 2) is attributable to increased local phenol and radical concentrations at the electrode surface, which raise the probability of sequential one-electron oxidation before the first radical has diffused away. This explains why the optimal current density of 10 mA/cm² is considerably lower than the maximum current density achievable with BDD in aqueous media (>100 mA/cm² for wastewater oxidation), confirming that synthetic electrolysis operates in a different

regime than oxidative waste treatment. The 34% cost advantage over Mn(OAc)₃ demonstrates the practical case for electrochemical synthesis beyond environmental considerations. As electricity from renewable sources continues to fall in cost and BDD electrode service lifetimes improve, the economic argument will strengthen further.

Conclusion

Electrochemical oxidative coupling of 4-tert-butylphenol was optimised across five anode materials and a range of operating conditions. BDD at 10 mA/cm², 25 °C, and 0.1 M TBABF₄ in 80:20 MeCN:water gave the best performance: 81.4% yield, 84.7% dimer selectivity, and 78.3% Faradaic efficiency. The BDD electrochemical route was 34% cheaper per mole than the conventional Mn(OAc)₃ process when oxidant, waste treatment, and energy costs were included. These results establish BDD electrosynthesis as a technically and economically competitive green alternative for oxidative phenol coupling, with direct scale-up potential given BDD's established manufacturability.

Acknowledgements

Funding Sources

Research was funded by institutional grants from the Universidad Azteca de Tecnología, Guadalajara, Jalisco, Mexico. No external funding was received.

Institutional Support

The authors thank the Department of Synthetic Chemistry, Universidad Azteca de Tecnología, for access to electrochemical workstations, GC-MS, HPLC, and the BDD electrode facility.

Contributions Not Qualifying for Authorship

Technical assistance from the electrochemistry laboratory staff in cell construction and instrument calibration is gratefully acknowledged.

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