

Ultrasonic Spray Fabrication of Copper and Ni NAC Gas Diffusion Electrodes

Materials process design expected outcomes and supporting literature for Sigracet 28 BC electrodes

Prepared for	Electrode development inquiry from a U.S. Department of Energy national laboratory
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Application	CO ₂ and CO electrolysis gas diffusion electrodes
Date	September 2026

Purpose

This white paper defines two separate spray-deposited electrode architectures: a 40-60 nm copper nanoparticle electrode and an SBA-15-derived Ni-NAC electrode. It consolidates published preparation methods, establishes a conservative ultrasonic spray starting window, and identifies the measurements required to demonstrate coating and electrochemical performance.

Scope

Published performance values are literature benchmarks, not guaranteed outcomes for a new MicroSpray process. The proposed operating windows are development starting points that require confirmation by mass loading, microscopy, gas transport, adhesion, and electrochemical testing.

Executive summary

The proposed program is technically well aligned with ultrasonic spray deposition because both electrode types use low-viscosity alcohol-based particle inks, small defined coating areas, and low total liquid volumes. The public record also matches the reported geometry closely: the national laboratory's patent application describes 10 mg Ni-NAC dispersed in 2 mL 2-propanol with Nafion, air-brushed onto a 3 x 3 cm Sigracet 28 BC sheet over a 1 x 1 cm active area. [1,3]

The first electrode uses 40-60 nm copper powder as the catalytic solid. The second uses Ni-NAC, an ordered mesoporous nitrogen-doped carbon containing atomically dispersed nickel. SBA-15 is used during catalyst synthesis as a removable silica pore template; it is etched away before electrode ink preparation. Therefore, the finished ink should be identified as Ni-NAC or Ni-N-C ordered mesoporous carbon, not as nickel-incorporated SBA-15. [1,3]

A 5 mg/mL solids concentration is the most defensible common starting point for the reported coupon volumes. At that concentration, 200 microliters deposited over 1 cm² and 800 microliters deposited over 4 cm² each provide 1.0 mg/cm² nominal loading before transfer losses. This aligns the two coupon sizes without changing the formulation. By contrast, 0.8 g/mL would correspond to 800 mg/mL solids and would not produce a thin catalyst layer. If 0.8 g/mL describes the bulk density of the complete ink rather than solids concentration, it is plausible but does not define catalyst loading.

Electrode	Catalyst function	Recommended starting ink	Recommended nozzle	Primary benchmark
Copper nanoparticle	CO or CO ₂ conversion toward C ₂ ⁺ products	5 mg/mL Cu in ethanol and 2-propanol; low ionomer fraction	120 kHz for fine coupons; 60 kHz for higher solids or scale-up	Uniform 0.5-1.5 mg/cm ² layer with preserved GDL transport
Ni-NAC	Selective CO ₂ -to-CO conversion	5 mg/mL Ni-NAC in 2-propanol with about 10 wt% Nafion relative to catalyst for literature comparison	60 kHz for micron-scale agglomerates; 120 kHz if dispersion is submicron and stable	Uniform 0.5-2.0 mg/cm ² layer; electrochemical performance compared with published Ni-NAC

Scientific and application context

Although the inquiry uses the phrase fuel cell application, the directly matching national laboratory work concerns CO₂ and CO electrolysis using gas diffusion electrodes. The architecture resembles fuel-cell catalyst-layer fabrication, but the device consumes electrical energy to convert CO₂ or CO into products rather than generating electrical energy from a fuel. This distinction matters when selecting the ionomer, electrolyte, catalyst loading, and validation test.

Luo and co-workers reported a generalized route to ordered mesoporous carbon containing isolated metal sites. Ni-NAC achieved up to 95% Faradaic efficiency for CO, maintained high selectivity at current density above 140 mA/cm², and was evaluated over 14 hours. The material had high surface area and ordered mesopores that improved site exposure and mass transfer. [1]

Yin and co-workers then coupled Ni-NAC with nanoscale copper nanowires. Ni-NAC generated CO, which enriched the local CO environment on copper and promoted carbon-carbon coupling. The optimized hybrid achieved 66% Faradaic efficiency to ethylene at more than 100 mA/cm² in an alkaline flow cell. This result supports a tandem Ni-Cu concept, but it does not establish that 40-60 nm copper powder will reproduce copper-nanowire behavior. [2]

Teng and Wang provide direct support for spray fabrication of copper nanoparticle electrodes on Sigracet 28 BC. They dispersed 400 mg Cu nanoparticles and 100 microliters of 5 wt% Nafion in 25 mL methanol, ultrasonicated for 2 hours, and air-sprayed the catalyst ink onto a reinforced Sigracet 28 BC GDL at 60 degrees C. Their work scaled from 5 cm² cells to a three-unit 50 cm² stack and reported approximately 80% C₂⁺ Faradaic efficiency at 500 mA/cm² across the optimized scale range. [4]

Substrate and coating requirements

Sigracet 28 BC is a 235 +/- 25 micrometer nonwoven carbon paper with a single-sided microporous layer and 5 wt% PTFE treatment. Reported MPL water contact angle is greater than 130 degrees, and MPL roughness is approximately 6.4 micrometers. [7] These properties favor alcohol-rich inks but also create a narrow process window: excessive wetting can drive catalyst into the pore structure, while overly rapid drying can produce edge accumulation and weak powdery deposits.

Property	Reported value	Process implication
Overall thickness	235 +/- 25 micrometers	Use flat vacuum or perimeter fixturing without crushing the GDL
Microporous layer	Single sided	Apply catalyst to the MPL side unless the cell design specifies otherwise
PTFE treatment	5 wt% in substrate	Avoid uncontrolled plasma or aggressive oxidation that changes hydrophobicity
MPL water contact angle	>130 degrees	Alcohol-rich carrier improves wetting relative to water-rich ink
MPL roughness	About 6.4 micrometers	Use multiple light passes to conformally cover the surface without pore sealing

Electrode type one copper nanoparticle catalyst layer

Materials

- Copper nanopowder with a nominal primary particle size of 40-60 nm and documented purity and oxide content.
- Ethanol and 2-propanol as the principal volatile carriers. Methanol is supported by published work but is not required for the initial MicroSpray screen.
- Ionomer or binder selected for the electrochemical cell. Nafion permits comparison with published recipes; an anion-exchange ionomer may be more appropriate for an alkaline membrane-electrode assembly.
- Sigracet 28 BC carbon paper, cut to 3 x 3 cm with a masked active area of 1 x 1 or 2 x 2 cm.
- Optional carbon-black or PTFE reinforcement layers only if flooding resistance or mechanical support is part of the experimental design.

Starting formulation

A baseline Cu concentration of 5 mg/mL makes the stated spray volumes directly comparable by area. Screen 5, 10, and 16 mg/mL if higher productivity is required; 16 mg/mL matches the Cu concentration used by Teng and Wang, although their carrier was methanol and their total sprayed volume was not specified. [4]

Component	Baseline	Development range	Reason
Cu nanoparticles	5 mg/mL	5-16 mg/mL	Controls deposited catalyst mass and suspension stability
Ethanol to 2-propanol	50:50 by volume	25:75 to 75:25	Balances wetting, evaporation rate, and handling
Ionomer solids to Cu	2.5 wt%	1.25-10 wt%	Provides cohesion while limiting active-site blockage
Water	Only that introduced by ionomer	Minimize unless required	Reduces copper oxidation and avoids excessive surface tension

Recommended process

1. Dry the GDL at 60-80 degrees C for 30 minutes, cool in a dry enclosure, record dry mass, and place MPL side up in a flat fixture.
2. Prepare the Cu dispersion under controlled ventilation. Add the ionomer after initial particle wetting, then sonicate with temperature control. Keep the dispersion sealed and use it promptly to limit oxidation and settling.
3. Mask the 3 x 3 cm coupon to expose either 1 x 1 or 2 x 2 cm. Use a hard shadow mask with minimal stand-off to obtain a reproducible boundary.
4. Start with a 120 kHz nozzle at 0.05-0.20 mL/min for the small coupons. Use 55-65 degrees C substrate temperature, 30-60 mm stand-off, 25-75 mm/s traverse speed, and 50-70% track overlap.
5. Apply alternating orthogonal raster passes. Permit the surface sheen to disappear between passes. Continue until the target delivered volume or gravimetric loading is reached.
6. Dry at 60 degrees C for 30-60 minutes under air or inert gas as appropriate. Do not add a high-temperature reduction step unless it is compatible with the GDL, ionomer, and intended copper oxidation state.

Expected outcome

The desired outcome is a continuous but porous copper catalyst layer with minimal agglomerate islands, no macroscopic rivulets, and no sealed regions of the MPL. Copper oxidation state is likely to influence selectivity, so XPS or equivalent surface analysis should be performed before and after electrochemical operation. Published copper nanoparticle and copper-nanowire results establish feasibility for C2+ formation but do not guarantee identical selectivity for commercial 40-60 nm Cu powder. [2,4]

Electrode type two SBA 15 derived Ni NAC catalyst layer

Material identity

Ni-NAC is produced by coordinating nickel with ethylenediamine and a carbon precursor in the pores of SBA-15, carbonizing the composite under argon at approximately 800 degrees C, and removing the silica template by etching. The final catalyst is an ordered mesoporous nitrogen-containing carbon with isolated nickel sites. The published material showed surface areas of roughly 720-930 m²/g across the M-NAC family and ordered pores of approximately 3.4-5.5 nm. [1]

The patent application reports an electrode ink containing 10 mg Ni-NAC, 2 mL 2-propanol, and 20 microliters of 5 wt% Nafion, sonicated for 60 minutes. The ink was air-brushed onto Sigracet 28 BC to coat a 1 x 1 cm region of a 3 x 3 cm sheet, followed by overnight air drying. [3] This is the closest public match to the inquiry.

Materials

- Fully synthesized, washed, neutralized, and dried Ni-NAC catalyst powder. No residual SBA-15 should remain except as a controlled impurity level.
- 2-propanol as the primary carrier, matching the patent example.
- Five wt% Nafion dispersion for direct literature comparison, or a cell-compatible anion-exchange ionomer in a second formulation branch.
- Sigracet 28 BC, cut and masked as described for the copper electrode.

Starting formulation

Component	Literature-matched value	MicroSpray starting value	Comment
Ni-NAC	10 mg in 2 mL	5 mg/mL	Exact concentration match to patent example
2-propanol	Primary carrier	Balance to volume	Low viscosity and compatible with Sigracet wetting
Five wt% Nafion solution	20 microliters per 10 mg catalyst	Same ratio for control	About 10 wt% ionomer solids relative to catalyst, assuming near-unity solution density
Dispersion treatment	60 min sonication	60 min with temperature control	Verify D90 and settling rather than relying on time alone

Recommended process

- Prepare and weigh the GDL as for the Cu electrode. Preserve the native PTFE/MPL state for the baseline test.
- Pre-wet Ni-NAC with a portion of 2-propanol, add the balance of solvent, and sonicate for 60 minutes with cooling. Add ionomer in a consistent sequence. Record visible settling over 30 and 60 minutes.
- Measure or estimate agglomerate size. Use a 60 kHz nozzle for micron-scale agglomerates or higher solids; use 120 kHz only when the dispersion remains stable and the feed path is comfortably larger than the largest agglomerates.
- Start at 0.10-0.40 mL/min, 55-65 degrees C substrate temperature, 30-60 mm stand-off, 20-60 mm/s traverse speed, and 60-75% overlap. Apply many light orthogonal passes.
- Maintain gentle reservoir agitation or low-shear recirculation during long runs. Avoid foam generation and avoid allowing solids to concentrate at the feed pickup.
- Dry in air overnight for direct comparison with the patent example. Add a shorter 60 degrees C dry as a separate process variable rather than changing both deposition and drying simultaneously.

Expected outcome

The desired coating is a porous, mechanically stable Ni-NAC layer with uniform nickel and nitrogen distribution across the active area and limited penetration through the MPL. The published catalyst provides a benchmark of approximately 95% CO Faradaic efficiency and high-rate operation, but reproducing those

values requires matched catalyst synthesis, ionomer content, loading, cell design, electrolyte, gas flow, and potential. [1,3]

Loading calculation and clarification of the reported ink value

Catalyst loading should be calculated from solids concentration, delivered volume, coated area, and measured transfer efficiency. Bulk liquid density alone cannot determine the catalyst mass deposited.

$$\text{Loading in mg/cm}^2 = \text{concentration in mg/mL} \times \text{delivered volume in mL} \times \text{transfer efficiency} / \text{coated area in cm}^2$$

Case	Delivered solids	Nominal loading	Interpretation
5 mg/mL; 200 microliters; 1 cm ²	1.0 mg	1.0 mg/cm ²	Recommended common baseline
5 mg/mL; 800 microliters; 4 cm ²	4.0 mg	1.0 mg/cm ²	Same areal loading on 2 x 2 cm
0.8 mg/mL; 200 microliters; 1 cm ²	0.16 mg	0.16 mg/cm ²	Very light catalyst layer
0.8 mg/mL; 800 microliters; 4 cm ²	0.64 mg	0.16 mg/cm ²	Same light loading on 2 x 2 cm
0.8 g/mL solids; 200 microliters; 1 cm ²	160 mg	160 mg/cm ²	Incompatible with a thin GDE layer
0.8 g/mL solids; 800 microliters; 4 cm ²	640 mg	160 mg/cm ²	Incompatible with a thin GDE layer

At 80% measured transfer efficiency, both 5 mg/mL baseline cases yield 0.8 mg/cm² actual loading. The test plan should therefore record both pump delivery and coupon mass gain. If the reported 0.8 g/mL value is the density of the complete ink, retain it as a fluid-property measurement and separately report catalyst solids in mg/mL.

Ultrasonic spray process rationale

Ultrasonic atomization forms droplets from capillary waves on a vibrating surface rather than using high liquid pressure to force an ink through a small hydraulic orifice. For particle suspensions, this supports low flow, low spray momentum, repeated thin passes, and reduced risk of a small pressure nozzle plugging. Stryckers and co-workers showed that ultrasonic spray parameters, ink composition, deposition temperature, and post-treatment can be used to control nanoparticle-layer thickness and morphology; they also attributed uniform layers to the narrow droplet distribution and acoustic deagglomeration associated with the process. [6]

For these electrodes, the main benefit is process control rather than a presumed intrinsic increase in catalyst activity. The method should be judged by deposited mass accuracy, within-area uniformity, overspray loss, pore preservation, and electrochemical reproducibility. A 120 kHz nozzle is preferred for fine low-solids Cu coatings on small coupons, while a 60 kHz nozzle provides greater tolerance for micron-scale Ni-NAC agglomerates and higher-throughput scale-up.

Development matrix

Variable	Level one	Level two	Level three	Response
Catalyst	Cu 40-60 nm	Ni-NAC	Optional tandem or layered control	Electrochemical product selectivity

Variable	Level one	Level two	Level three	Response
Solids concentration	5 mg/mL	10 mg/mL	16 mg/mL Cu only	Stability, loading rate, morphology
Areal loading	0.5 mg/cm ²	1.0 mg/cm ²	2.0 mg/cm ²	Coverage, resistance, gas transport
Substrate temperature	45 degrees C	60 degrees C	75 degrees C	Drying front, penetration, adhesion
Nozzle frequency	60 kHz	120 kHz	Not applicable	Droplet field and slurry tolerance
Pass orientation	Single direction	Alternating 90 degrees	Rotated 45 degrees	Coating uniformity
Ionomer ratio	Low	Literature matched	High	Adhesion versus blocked active area

A fractional factorial screen can reduce the number of coupons, but catalyst identity, loading, and ionomer chemistry should not be confounded in the first comparison. Duplicate coatings are acceptable for process setup; triplicate electrochemical specimens are preferred for reporting.

Characterization and acceptance criteria

Test	Purpose	Suggested acceptance criterion
Gravimetric mass gain	Actual catalyst-plus-binder loading	Within +/-10% of target after drying
Mass or elemental map	Within-area uniformity	No edge banding; coefficient of variation below 10-15%
Optical microscopy	Macroscopic defects	No rivulets, bare islands, mask leakage, or loose powder
SEM and EDS	Layer morphology and Cu or Ni distribution	Continuous porous coverage without pore sealing
Contact angle	Change in surface wetting	Documented and consistent; no uncontrolled collapse of hydrophobicity
Gas permeability or pressure drop	GDL transport preservation	No material loss relative to the application-defined limit
Tape or controlled rub test	Relative cohesion	No gross delamination; method recorded for comparison
XPS for Cu	Cu oxidation state	State quantified before and after electrolysis
Electrochemical testing	Activity, selectivity, and durability	Faradaic efficiency, current density, cell voltage, and stability reported together

Scale up from 2 to 100 cm²

Scale-up should hold areal loading, wet-pass density, substrate temperature, and track overlap constant rather than holding only total liquid volume constant. The deposition path should include edge overscan so the spray plume reaches steady state before entering the active area. For large areas, continuous agitation

and timed mass checks are more important because settling and solvent evaporation can change the feed concentration during the run.

- Use a fixed deposited-mass target in mg/cm² and calculate total solids from active area.
- Maintain the same delivered liquid per unit area and the same dry time between pass groups.
- Map temperature across the platen; large-area nonuniformity often reflects thermal gradients rather than atomization alone.
- Qualify the center and all four quadrants by mass or elemental mapping before electrochemical testing.
- For production, close the loop with pump calibration, reservoir mass, coupon mass gain, and recorded motion parameters.

Safety and handling

Copper nanopowder and dry Ni-NAC should be handled as respirable particulate hazards using enclosed transfer, local exhaust, suitable respiratory protection where required, grounded equipment, and controls for combustible dust. Ethanol, 2-propanol, and methanol are flammable; spraying increases vapor generation and must be performed in appropriately rated ventilation away from ignition sources. Copper nanopowder can oxidize during storage and dispersion. Use supplier safety data sheets, limit batch size, prevent static discharge, and do not return used material to the original container.

Hydrofluoric acid is used in the published Ni-NAC synthesis to remove SBA-15. HF handling is outside the electrode-spraying operation and requires a dedicated institutional procedure, specialized PPE, trained personnel, and emergency controls. Only fully washed, neutralized, and dried catalyst should enter the spray process. [1,3]

Published outcomes and their relevance

Source	Published outcome	Relevance to this program	Limitation
Luo et al. 2022	Ni-NAC reached 95% CO FE; high FE above 140 mA/cm ² ; 14 h study	Defines Ni-NAC material benchmark	Does not validate the proposed MicroSpray parameters
Yin et al. 2022	Ni-NAC plus Cu nanowires reached 66% ethylene FE above 100 mA/cm ²	Supports tandem Ni-Cu chemistry	Copper morphology was nanowire, not 40-60 nm powder
US20240295038A1	5 mg/mL Ni-NAC in IPA/Nafion air-brushed onto 1 cm ² of Sigracet 28 BC	Direct match to substrate, geometry, and ink family	Published application; airbrush rather than ultrasonic nozzle
Teng and Wang 2025	Cu NP ink air-sprayed on Sigracet 28 BC; optimized C2+ FE near 80% at 500 mA/cm ² across scale range	Direct precedent for Cu spray deposition and scale-up	Cu particle size not identified as 40-60 nm in the article text
Stryckers et al. 2016	Uniform nanoparticle layers produced by ultrasonic spray	Supports morphology control and particle-layer deposition rationale	Not an electrochemical GDE study

Patent landscape

US 2024/0295038 A1, Metal-impregnated carbon materials, is the most directly relevant patent publication. It names Long Qi, Wenyu Huang, Sen Zhang, Zhouyang Yin, Lun An, and Kanika Lalit as inventors and includes claims directed to mesoporous carbon matrices containing metal sites, electrochemical CO₂ reduction, electrolytic cells, and methods of making the material. Its examples disclose the Sigracet 28 BC electrode

preparation summarized above. Google Patents reported the application as pending when this paper was prepared. [3]

US 12,508,580 B2, Atomically dispersed metal catalysts and applications thereof, is adjacent background art rather than a patent on the national laboratory's Ni-NAC/SBA-15 route. It concerns nitrogen-doped carbon materials with atomically dispersed transition-metal sites and includes fuel-cell applications. It is relevant to freedom-to-operate review for broader single-atom M-N-C catalyst programs but does not establish ownership of the proposed ultrasonic spray parameters. [8]

This summary is technical information, not a legal opinion. A formal freedom-to-operate analysis should compare current claims, prosecution history, jurisdiction, catalyst synthesis, electrode composition, and the exact commercial process.

Conclusions

Two separate ultrasonic-sprayed electrodes are technically justified: a Cu nanoparticle GDE and a Ni-NAC GDE. The strongest common starting condition is 5 mg/mL catalyst solids, which converts the reported 200 and 800 microliter spray volumes into the same nominal 1 mg/cm² loading on 1 and 4 cm² active areas. Copper should begin with the 120 kHz nozzle for fine, low-solids coating, while Ni-NAC should begin with the 60 kHz nozzle if micron-scale agglomerates are present. Both should be applied as many light, overlapping, alternating raster passes onto the heated MPL side of Sigracet 28 BC.

The first experimental milestone is not maximum electrochemical activity; it is reproducible deposited mass, uniformity, adhesion, and preservation of GDL transport. Once those conditions are established, electrochemical testing can determine whether ultrasonic deposition matches or improves on the air-brushed literature controls. The public record supports the catalyst systems and substrate architecture, while the MicroSpray process itself remains a development variable to be validated.

References

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