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Formulation of Conductive Inks for DIW Printed Battery Electrodes

P. Lawson, M. C. Freyman, S. Chandrasekaran

August 23, 2024

Disclaimer

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

Instructions

This 300 word length abstract should generally summarize your SULI experience. This summary should highlight research accomplishment(s), be written at a level approachable by a broad and largely non-subject matter expert audience (Scientific American level of sophistication), describe Department of Energy programmatic or mission relevance of your activities, define the institutional setting, and generally discuss activities, outcomes, impacts, lessons learned, and professional growth and development resulting from your appointment. Submission of required materials must be made prior to the end of their appointment and as directed by the host laboratory. Host institutions will provide instructions regarding use of the online submission system.

General Audience Abstract

As society shifts away from fossil fuels, we require better batteries for many diverse applications to enable energy storage and de-carbonization. Our group's focus is particularly on optimizing Li-ion battery electrodes for low temperature applications by 3-D printing the cathodes into high surface area shapes. Ion transport can be a major problem in batteries at low temperatures, so optimizing for ion transport can help combat these issues. By making the cathodes highly conductive and with high surface area, ion transport through the battery is improved. There are many possible formulations for conductive printable inks, and I focused on improving two known base formulations. The first is based on the conductive polymer PEDOT:PSS dispersed in water and dimethyl sulfoxide. Graphene nano platelets (GNP) were added to this ink at various ratios, which was able to increase conductivity over tenfold. This ink has the benefit of very high conductivity, good mechanical strength, and mild processing conditions. Its main problems are shrinkage as it drys, polymer agglomerations which can clog the printing nozzle and lower porosity. An alternative ink of single layer graphene oxide (SLGO) emulsified with water, toluene, octadecyl amine, and hydroxypropyl methylcellulose which forms graphene aerogel upon carbonization was also investigated. It has the benefit of very high porosity with an accessible open pore structure, large surface area, and low shrinkage. However these graphene aerogel parts are slightly less conductive and not as mechanically durable as the GNP polymer parts.

This work was funded by LDRD 23-SI-002. This work was supported in part by the U.S. Department of Energy, Office of Science, Office of Workforce Development for Teachers and Scientists (WDTS) under the Science Undergraduate Laboratory Internships Program (SULI). This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

Formulation of Conductive Inks for DIW Printed Battery Electrodes

Abstract

Ink formulations for DIW printing of Li ion battery electrodes were optimized for high conductivity, surface area and printability. Our focus is particularly on optimizing Li-ion battery electrodes for low temperature applications by 3-D printing the cathodes into high surface area shapes. The sluggish kinetics of ion transport at the solid-electrolyte phase boundary can be a major problem in batteries at low temperatures, so optimizing for ion transport can help combat these issues. Two families of DIW ink were investigated; aqueous conductive polymer suspension with graphene nano platelets (GNP) ink, and “oil in water” graphene oxide (GO) micro emulsion ink which carbonizes to an open cell graphene aerogel. By iterative formulation changes, the conductivity of PEDOT:PSS based ink was increased over tenfold, and stiffness of GO emulsion ink was increased to provide better printability without sacrificing porosity.

Introduction

Electronics have become central to society as we know it, and each device we use needs a power source. Batteries are expected power our devices reliably in a broad range of environmental conditions, but conventional Li ion batteries struggle in extreme conditions, especially subzero temperatures. With less thermal energy in the battery cell, ion transport kinetics become sluggish as diffusion and solubility of Li ions are negatively affected when electrolyte is cold. Charge transport across the electrode/electrolyte phase boundary is also impacted, causing polarization and lower coulombic efficiency.[1] Our group is working to combat poor battery performance at low temperatures by optimization of the electrodes specifically for these conditions. 3D printing of battery cathodes presents a promising method for creating complex geometries to help improve slow ion transport at low temperatures and increase performance.

Highly conductive electrodes with a greater surface area and short ion diffusion path lengths help to minimize the negative effects of sluggish Li ion transport. By direct ink write (DIW) 3D printing, topologically optimized geometries can be printed, and solvents or templating agents can be removed after printing to give highly porous structures.[2] These advanced structures can outperform simpler cathode designs by optimizing charge transport paths and increasing the electrode surface area.[3]

For this project, we investigated two families of DIW printing inks. The first ink is based on the conductive polymer poly(3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT:PSS) , chosen for its conductivity, water solubility, and mechanical resilience. PEDOT:PSS has been used in literature for DIW printing [4,5,6] and PEDOT:PSS with GNP has been used for thin film capacitors [7] and organic light emitting diodes (OLEDs)[8] but their combined use in DIW printing is our novel contribution. This ink allows for gentle post-processing treatments since the polymer binder is conductive and does not need to be removed by high temperature carbonization treatments. By not treating these electrodes at high temperatures, warping, fissures, and other damage can be avoided. The polymer also makes the parts flexible and mechanically durable. Graphene nanoplatelets (GNPs) are added to significantly enhance the conductivity, forming a conductive network throughout the polymer and increasing conductivity more than tenfold.

The second ink is based on an “oil-in-water” emulsion of graphene oxide (GO). This ink was selected for the high surface area and open pore structure of the finished parts reported in literature. Ultra-low density graphene aerogels have been reported by carbonization of these inks.[2,9] However, to achieve ultra-low density, stiffness has been sacrificed which limits the detail and complexity of parts which can be printed by DIW methods. We focused on retaining the desirable properties of the finished parts while increasing viscosity to enable printing more intricate structures.

Materials and Methods

PEDOT:PSS + GNP Ink

PEDOT:PSS was received as an aqueous solution (Heraeus Clevios PH1000 1.0-1.3%) and sonicated 30 minutes before freeze drying to create more concentrated solutions (froze on dry ice -78°C, vacuum of <0.1 tor for 3 days) All other materials used as received. Solids content of inks were recorded as a percentage w/v of the solvent volume. Various percentages were tested from 4.5-8.0% PEDOT:PSS and 2-20%GNP. Solids were then hydrated with a mixed solvent of 85% DI water and 15% DMSO by volume. These mixtures were mixed at 2500 rmp in 1 min intervals in a FlackTec planetary mixer until well mixed (5-8 min). Two post processing procedures were compared, immediate freezing on dry ice for freeze drying, or heated drying by first drying at rt in air over night, then at 70°C over night and 130°C for 90 min.

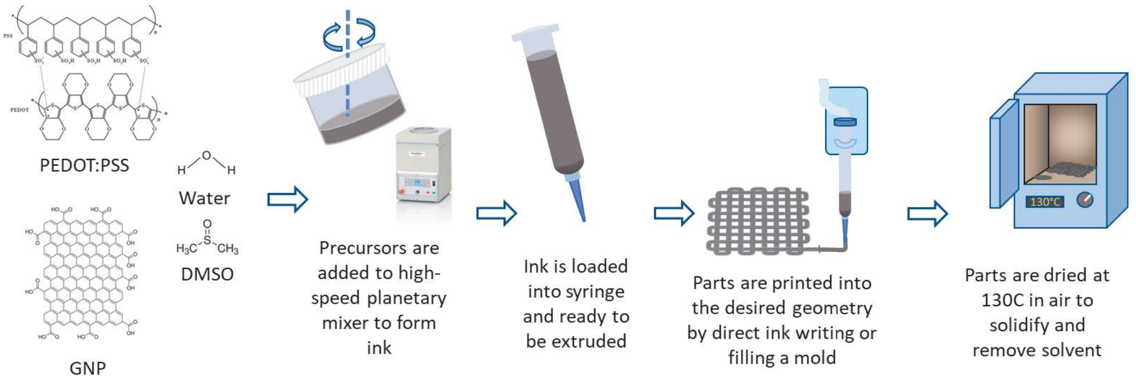


Figure 1: General processing steps for PEDOT:PSS + GNP ink parts to make polymer electrodes

GO Emulsion Aerogel Ink

Emulsions were prepared by suspending carboxyl rich single layer GO (1-20 µm sheets from CheapTubes) in deionized water at desired concentration, then mixing in desired binder (HPMC, CNC, CMC, Pluronic or PEDOT:PSS) to form the aqueous phase. Octadecyl amine (ODA) was then dissolved in toluene or heptane to prepare the organic "oil" phase. Each emulsion used 80% (4.0mL) of aq. phase and 20% (1.0mL) org. phase. The phases were emulsified by a high speed helical wire impeller (consumer grade milk frother) Post processing consisted of immediate freezing on dry ice for freeze drying, then a carbonization procedure at 1050°C for 3 hr in a tube furnace under dry nitrogen gas.

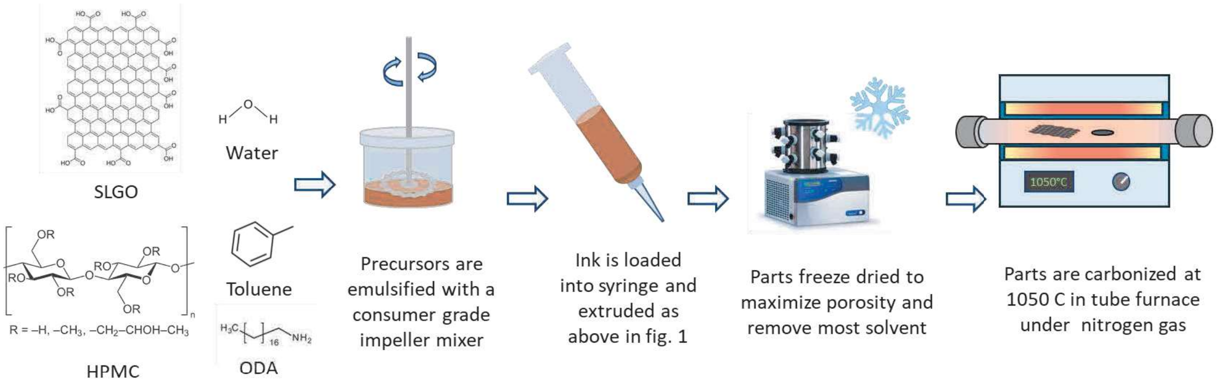


Figure 2: General processing for GO Emulsion ink to make graphene aerogels electrodes

Each ink was loaded into 10mL syringes for printing and centrifuged at 2000rpm for 2 min to remove air bubbles or solid inclusions. Parts were printed on an AeroTech printer and extruded by pneumatic pressure with 400µm or 200µm nozzles. Pressure needed varied per print from 6psi to 21psi. Test prints consist of a 12.8mm square lattice with one layer each in the x and y directions at a road width of 0.8mm and layer height of 0.26mm. Rheology was measured on a TA Instruments Discovery Hybrid Rheometer with 20mm Peltier plate geometry and a 500µm gap.

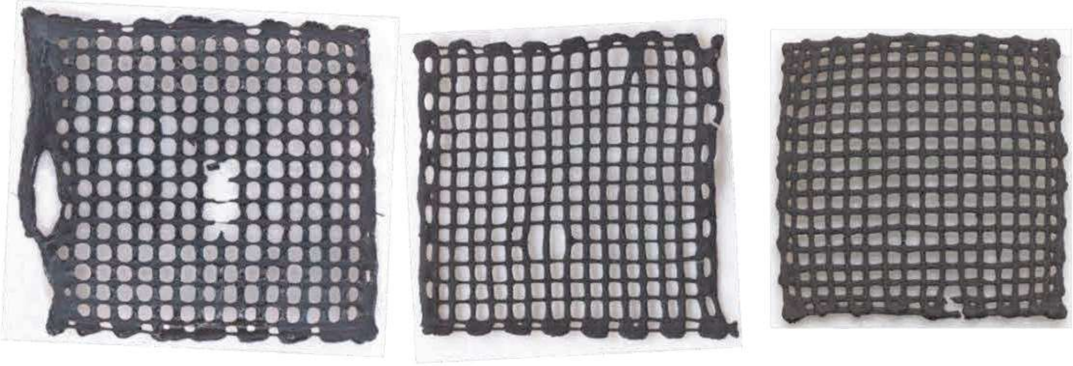
Bulk conductivity measurements were measured using a 2-point probe multimeter configuration with probes 5mm apart on a 10 mm wide circular pellet. Electrochemical measurements were made in a 3 electrode configuration with a SCE reference electrode and a platinum wire counter electrode in 3.0M LiCl aq. Rectangular working electrodes were cast from the ink formulations in a rubber sheet mold on glass 2x10x20 mm.

Results and Discussion

PEDOT:PSS + GNP Ink

Aqueous suspensions of PEDOT:PSS (5%-8% w/v PEDOT:PSS in 15 DMSO : 85 Water) have been previously reported to make printable conductive DIW inks.[4,6] Unfortunately these are not conductive enough for our desired application of low temperature cathodes. GNP was selected as a highly conductive additive to the PEDOT:PSS ink system. Carbon nanofibers were also tested in a PEDOT:PSS ink, but their addition resulted in unfavorable agglomeration and stringy behavior which inhibited printing by our methodology.

At high solids loading of PEDOT:PSS, the polymer aqueous suspension unfortunately begins to destabilize and agglomerate. To achieve a printable consistency 6wt% PEDOT:PSS was used, which is at the cusp of forming these agglomerations which can clog the print head and slow down printing. Some of these issues can be seen in the printed parts of fig. 3 with skips or inconsistency of line width. 3mm ceramic grinding media were added to the ink during rotary mixing and speed was increased to 3500rpm in an attempt to improve consistency and break up agglomerates, but this didn't provide any measurable improvement. The most successful adjustment to our pre-processing approach was to add desired quantity of GNP directly to a measured quantity of commercial PEDOT:PSS solution and sonicate them together for one hour before freeze drying. This mixture rehydrated more smoothly than weighing out dried PEDOT:PSS separately. Inks were used soon after mixing whenever possible, as agglomeration worsens in storage whether refrigerated or at room temperature.


0% GNP 6% PEDOT

6% GNP 6% PEDOT

12% GNP 6% PEDOT

Figure 3: Optical microscope images of printed polymer lattice electrodes, with the ink concentration of PEDOT:PSS and GNP under each.

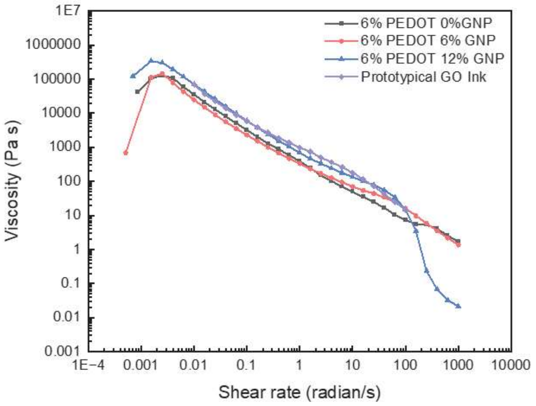


Figure 4: Rheology of three PEDOT:PSS inks

Rheology plot in fig. 4 shows the shear thinning behavior of the PEDOT:PSS based inks. Shear thinning is a crucial property of DIW inks, as it allows ink to flow easily when being pushed through the nozzle, but keep their shape once extruded. The ink with 12% GNP and 6% PEDOTP:PSS had the best shear thinning behavior, as it was stiff at low shear rates but thinned more at high shear rates. These were compared to a GO based ink we know to print well on our Aerotech printing setup.

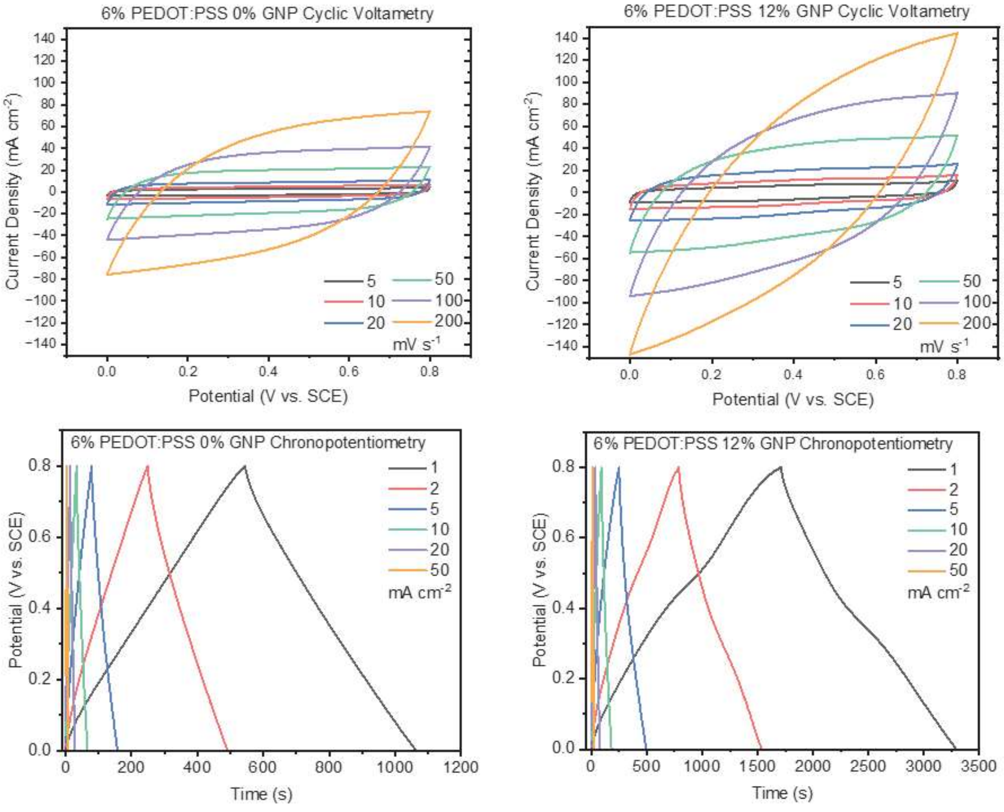


Figure 5: Electrochemical data for two 6% PEDOT:PSS inks, without GNP (left) and with 12% GNP (right).

In fig. 5 cyclic voltammetry (top) shows that addition of GNP increased the current density in the same potential range. Chronopotentiometry (bottom) shows only electrochemical double layer capacitance in the PEDOT:PSS only ink, with additional pseudocapacitive behavior in the 12% GNP ink demonstrated by the non-linear curves. Below in fig. 6 are resistance measurement collected on various samples for comparison. 6% PEDOT:PSS and 12% GNP in 15:85 DMSO aq. gave the lowest resistance value.

Sample Name	Resistance
100% GNP dry pressed	6 Ω
6% PEDOT:PSS air dried	50 Ω
6% PEDOT:PSS 130C cured	90 Ω
4.5% PEDOT:PSS 2% GNP air dried	4 Ω
4.5% PEDOT:PSS 2% GNP 130C cured	3 Ω
6% PEDOT:PSS 12% GNP 130C cured	2 Ω
Carbonized 2%HPMC 2%GO 2% ODA	40 Ω

Figure 6: Preliminary conductivity data measured by multimeter and two point probe with 5mm spacing

GO Emulsion Aerogel Ink

The prototypical emulsion ink is based on an emulsion of water and toluene, utilizing ODA and GO as emulsifiers.[9] By increasing the solid loading of the ink and adding hydroxypropyl methylcellulose (HPMC), we achieved a much stiffer and more printable viscosity. Carboxylate-rich graphene oxide single layers served as both the conductive component and the emulsifier in the “oil-in-water” emulsion. The graphene nanoplatelets orient themselves along the phase boundary between the aqueous and organic phases of the emulsion system, driven by dipole-dipole interactions of water with the carboxylate groups, nonpolar interactions with the organic phase, and π-π stacking when an aromatic solvent is used. Octadecyl amine works as a ligand which decorates the polar carboxylate groups to decrease overall dipole of GNPs and better equalize the affinity for the two phases.

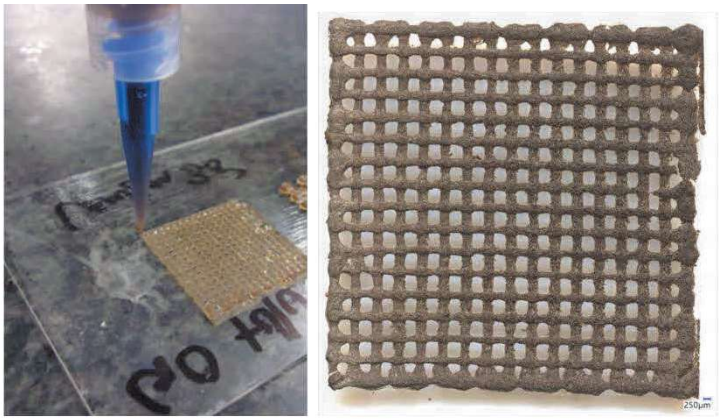


Figure 7: GO Emulsion ink during printing and after freeze drying

We investigated the behavior of several viscosity increasing additives to achieve a more printable GO emulsion ink. PEDOT:PSS was added to the aq. phase with the other emulsion precursors and helped viscosify the aq. phase, but when toluene was added the polymer immediately coagulated in lumps which clogged nozzles upon attempting to print. Sodium carboxymethylcellulose (CMC), nanocrystalline cellulose (CNC) and polyoxypropylene polyoxyethylene copolymer (Pluronic) were each tested at 2% w/v of the aqueous phase, but none gave a satisfactory improvement to viscosity. These results can likely be explained by the intermolecular forces and zeta potential between each viscosifier and the two phases of the emulsion. CMC may be too polar for good interaction with the organic phase, while Pluronic seemed to make the ink almost doughy and lose much of its surface tension.

Hydroxypropyl methylcellulose (HPMC) gave the best increase in viscosity, and afforded quality parts upon post processing. The best performing ratio tried was an aq. phase of 2wt% GO + 2wt% HPMC and an organic phase with 2wt% ODA with 80% aq and 20% org. This is the formulation being printed about in fig. 7 As a long polymer chain which can have polar and non-polar interactions both stabilizes and greatly thickens the emulsion. The addition of HPMC also mitigates the necessity of using toluene as the organic phase, as heptane based inks with added HPMC have comparable printability to toluene based inks of otherwise the same composition. This opens up the possibility for alternative nonpolar solvents as greener replacements to toluene. At low concentration of GO and HPMC, n-heptanes and mineral oil both failed to provide sufficient viscosity to the emulsion, however at increased solids concentration (2wt% GO + 2wt% HPMC in aq., 2wt% ODA in org., 80:20 aq:org) little difference was seen between emulsions with toluene or heptane organic phases.

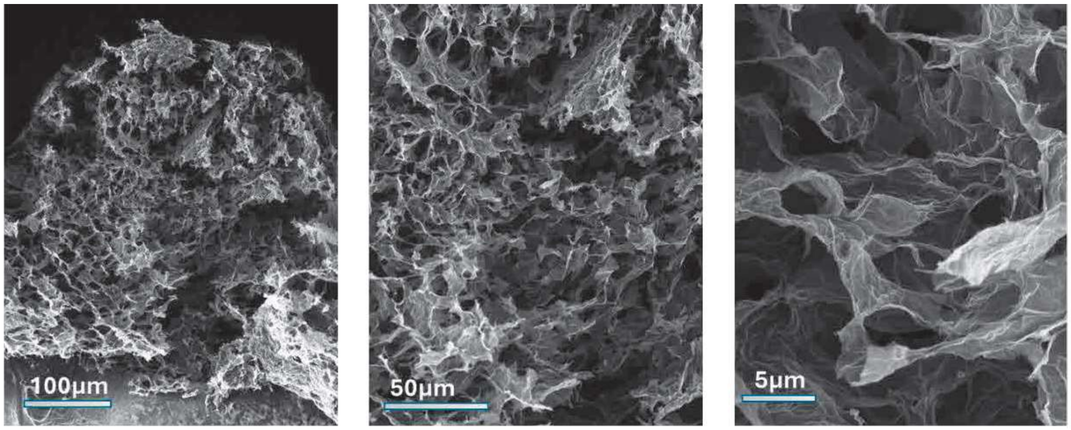


Figure 8: SEM Images progressively zoom in on carbonized GO emulsion aerogel part. GO Emulsion gave large, deep, and accessible pores in a variety of length scales.

Scanning electron microscope (SEM) images in fig 8 of the emulsion inks after freeze drying and carbonization demonstrate the low density open pore structure of the aerogel. During carbonization the samples lose over 80% of their post freeze-dry mass to make a low-density structure of 0.007 g cm^{-3}

The GO emulsion ink exhibits a robust pore structure with a wide range of micro and meso pores. By freeze-drying then carbonizing this ink, the pores can be maintained in the finished parts. Carbonized parts are prone with breakage upon rough handling, but can be handled enough for gentle coating or device fabrication.

Conclusions

Overall, these advancements in DIW printing ink formulation offers improvements in printability, porosity and conductivity. Addition of GNP to PEDOT:PSS inks was able to greatly increase their conductivity, and addition of HPMC to GO Emulsion inks favorably increased their viscosity, stiffness and working properties. Both ink formulations show promise for use as high performance electrode materials. PEDOT :PSS + GNP could be preferred for its conductivity, mild post processing and duribilty, but lacks in porosity. Carbonized GO emulsions could be preferred however for maximized surface area to facilitate efficient ion transport at the phase boundary. By making highly conductive electrodes with great surface area, charge transport both across the solid-electrolyte interface and through the solid phase current collector can be improved to help combat the poor charge transport kinetics at low temperatures. Further work in this area is required in decoration of these printed electrodes in electroactive material like gamma MnO2 which would be necessary before testing in complete Li ion battery cells.

Acknowledgements

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Developing Printable Conductive Inks for Energy Storage

Direct Ink Writing formulations of flexible conductive polymers and carbon nanomaterials

Preston Lawson38
Summer Intern from CSU Chico
Supervised by Megan Freyman1

June-Aug 2024

LLNL-PRES-XXXXXX

Lawrence Livermore National Laboratory

SULI Program

- Science Undergraduate Research Internship (SULI)
- Available at all DOE national labs
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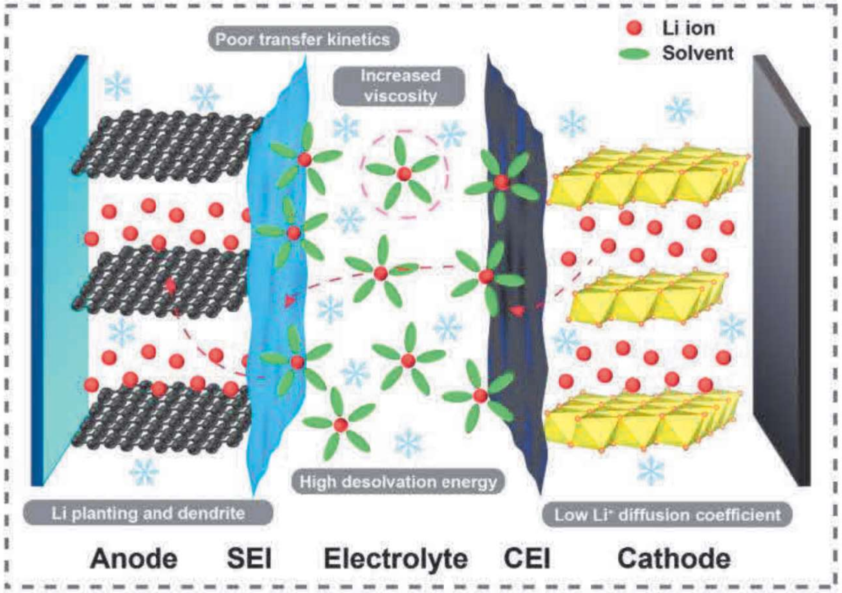
U.S. DEPARTMENT OF ENERGY | Office of Science

Low Temp Li Ion Batteries

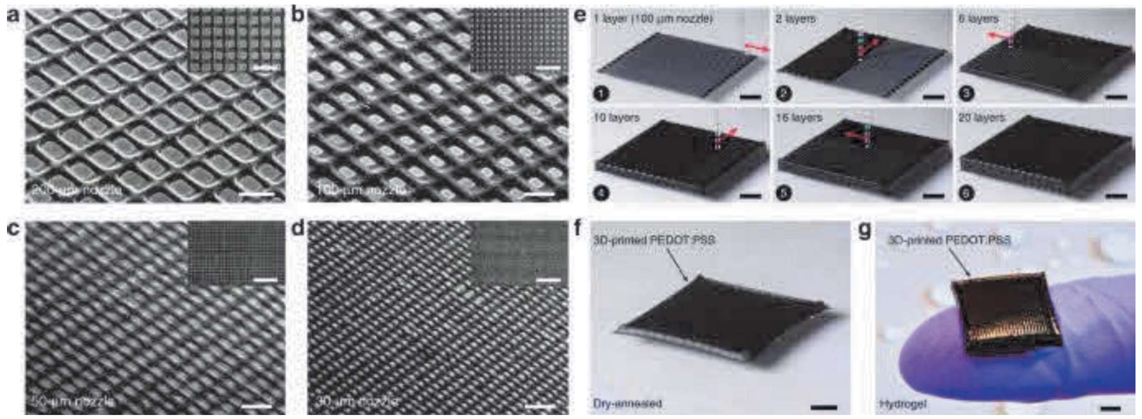
- Project goals: 3D print electrodes optimized for low temp Li batteries
- Li batteries have poor performance in extreme conditions like cryogenic temp

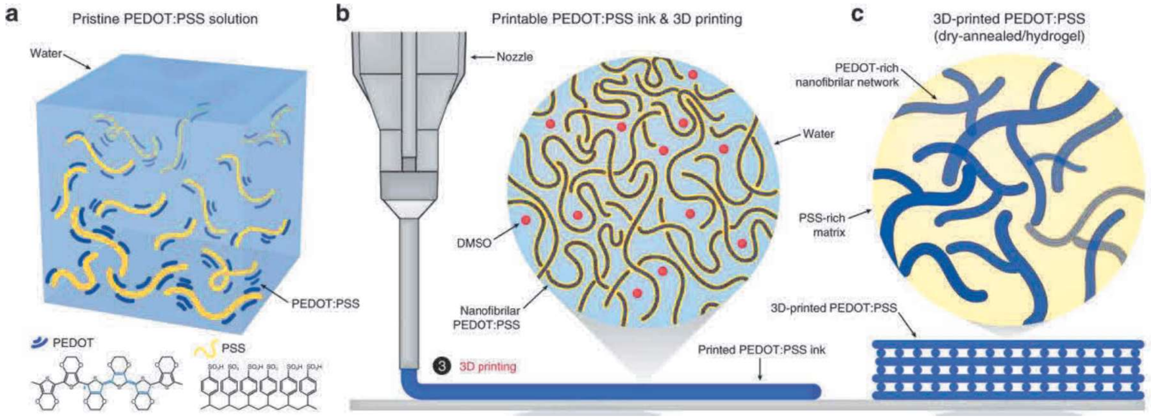


- Sluggish kinetics/ion transport at low temp

Luo, H.; Wang, Y.; Feng, Y.-H.; Fan, X.-Y.; Han, X.; Wang, P.-F. Lithium-Ion Batteries under Low-Temperature Environment: Challenges and Prospects. Materials 2022, 15 (22), 8166. https://doi.org/10.3390/ma15228166.

Ink 1 - PEDOT:PSS Ink Literature Basis



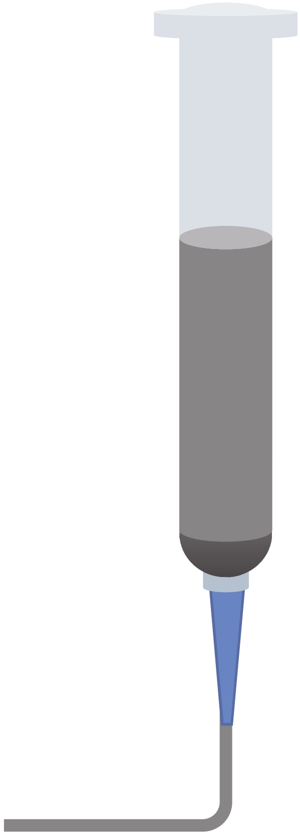


Starting from literature papers

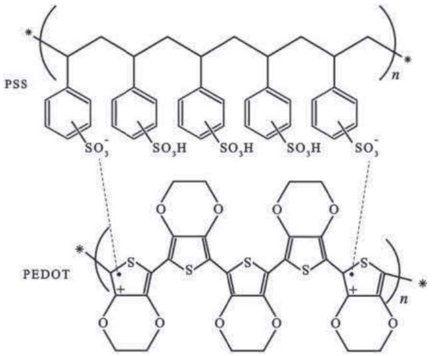
Yuk, H., Lu, B., Lin, S. et al. 3D printing of conducting polymers. Nature 11, 1604 (2020). https://www.nature.com/articles/s41467-020-15316-7

Polymer Direct Ink Write (DIW) Printing

- Conductive polymer DIW 3D Printing
- Mild post processing
- No insulating precursors need to be carbonized or burned off
- Avoid damage to delicate geometries from high T carbonization

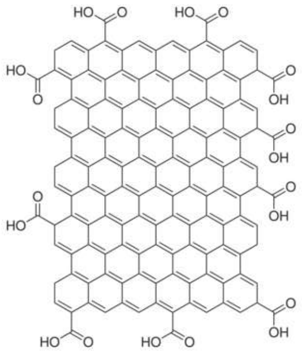


PEDOT:PSS Prep



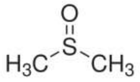
PEDOT:PSS

(Poly 3,4-ethylenedioxythiophene: polystyrene sulfonate)

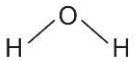


GNP

(Carboxyl rich graphene nano-platelets)

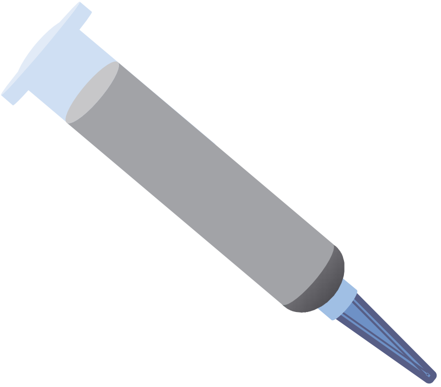


DMSO



Water

Precursors are added to high-speed planetary mixer to form ink

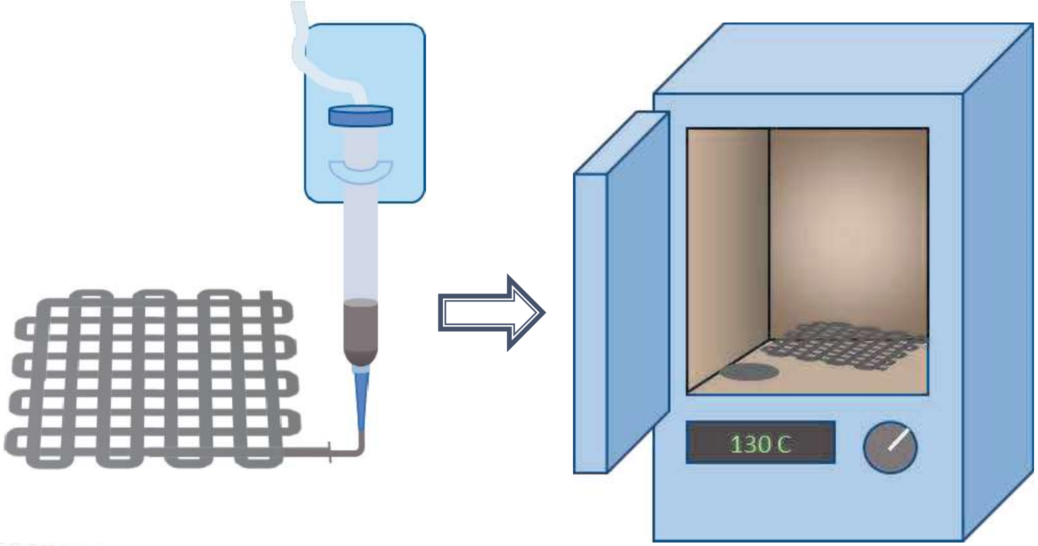


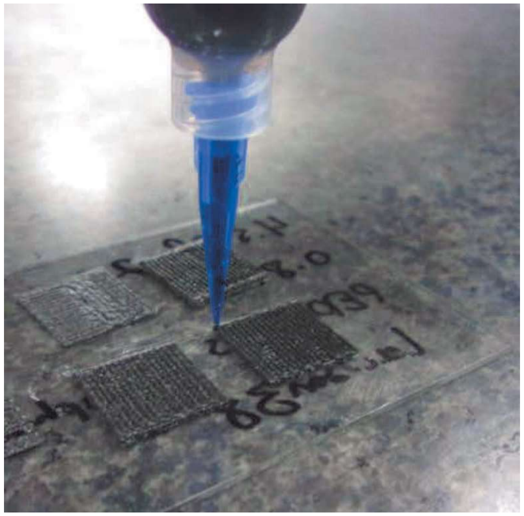
Ink is loaded into syringe and ready to be extruded

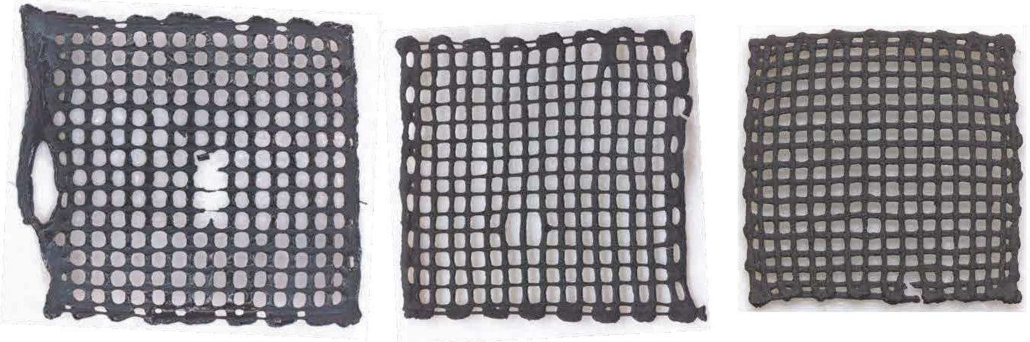
E.g. formulation: 60mg PEDOT:PSS, 120mg GNP, 850uL water, 150uL DMSO

PEDOT:PSS Parts

- Initial print tests at 6.5 psi with 400um nozzles.
- Simple disk mold for conductivity tests
- Mild annealing at 130C in air





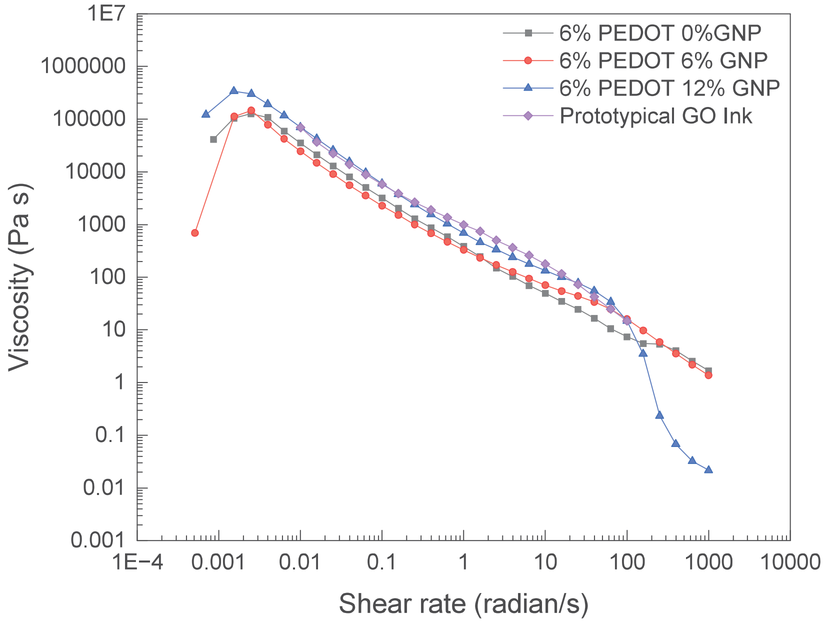

0% GNP 6% PEDOT:PSS
6% GNP 6% PEDOT:PSS
12% GNP 6% PEDOT:PSS

Lattices during printing and after curing

Rheology

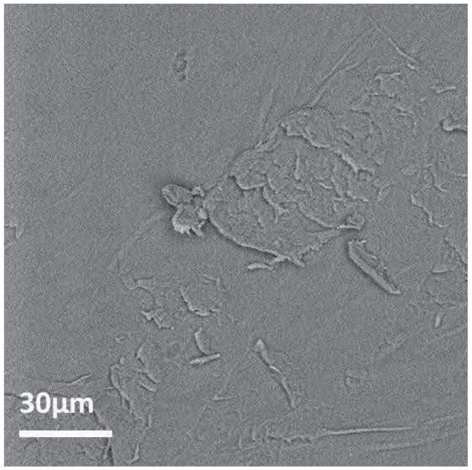
- Measures viscosity, very useful for 3-D print inks
- Uses spinning plate and force meter to measure shear thinning

Measured on a Pelletier plates DHR Rheometer

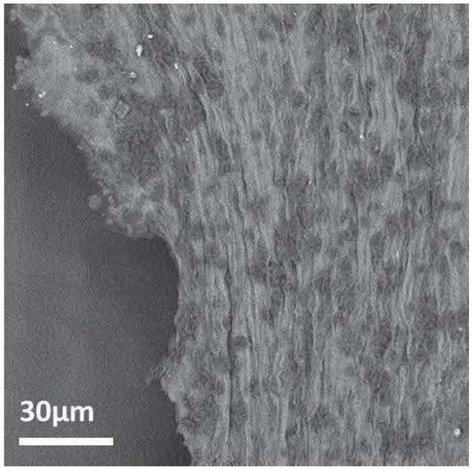


Shows enough shear thinning to flow out of printer, but stay put after extrusion

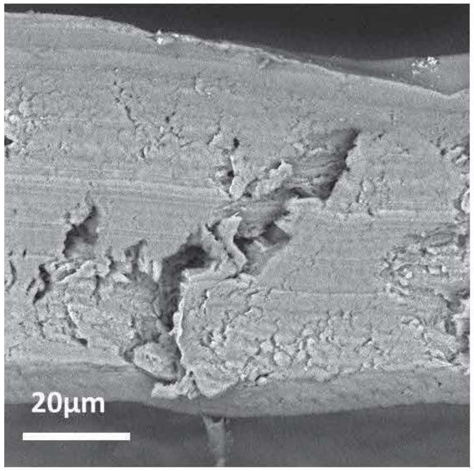
SEM Images of PEDOT:PSS



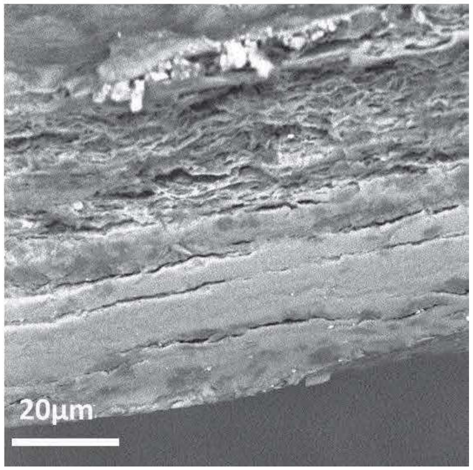
A. 6% PEDOT:PSS top view



C. 4.5% PEDOT:PSS 2% GNP top view



B. 6% PEDOT:PSS cross section

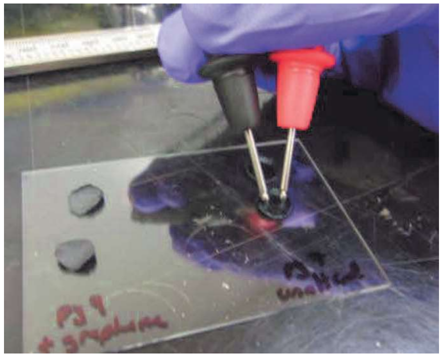


D. 4.5% PEDOT:PSS 2% GNP cross section

- Comparison of annealed PEDOT:PSS part with or without GNP
- GNP appears to migrate to the surface during drying

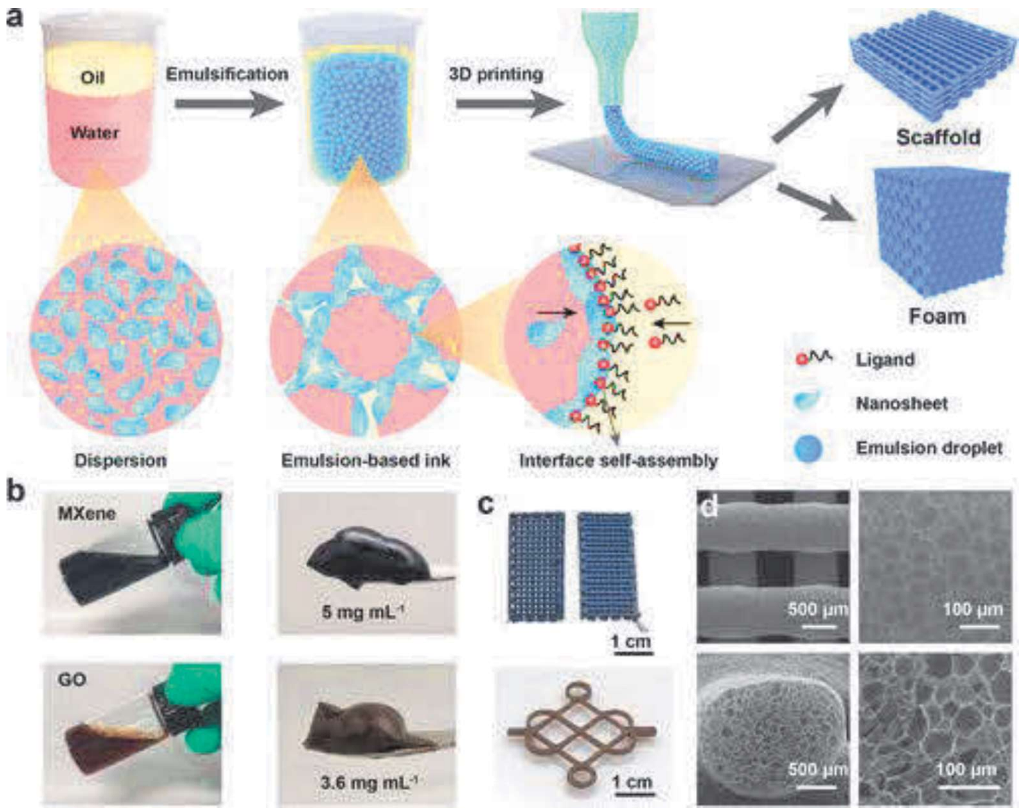
Ink Conductivity

Preliminary conductivity measurements show that GNP increases conductivity by an order of magnitude +.



Sample Name	Resistance
6% PEDOT:PSS air dried	50 Ω
6% PEDOT:PSS 130C cured	90 Ω
4.5% PEDOT:PSS 2% GNP air dried	4 Ω
4.5% PEDOT:PSS 2% GNP 130C cured	**3 Ω**
100% GNP dry pressed	6 Ω

Ink #2 GO Emulsion Literature Basis

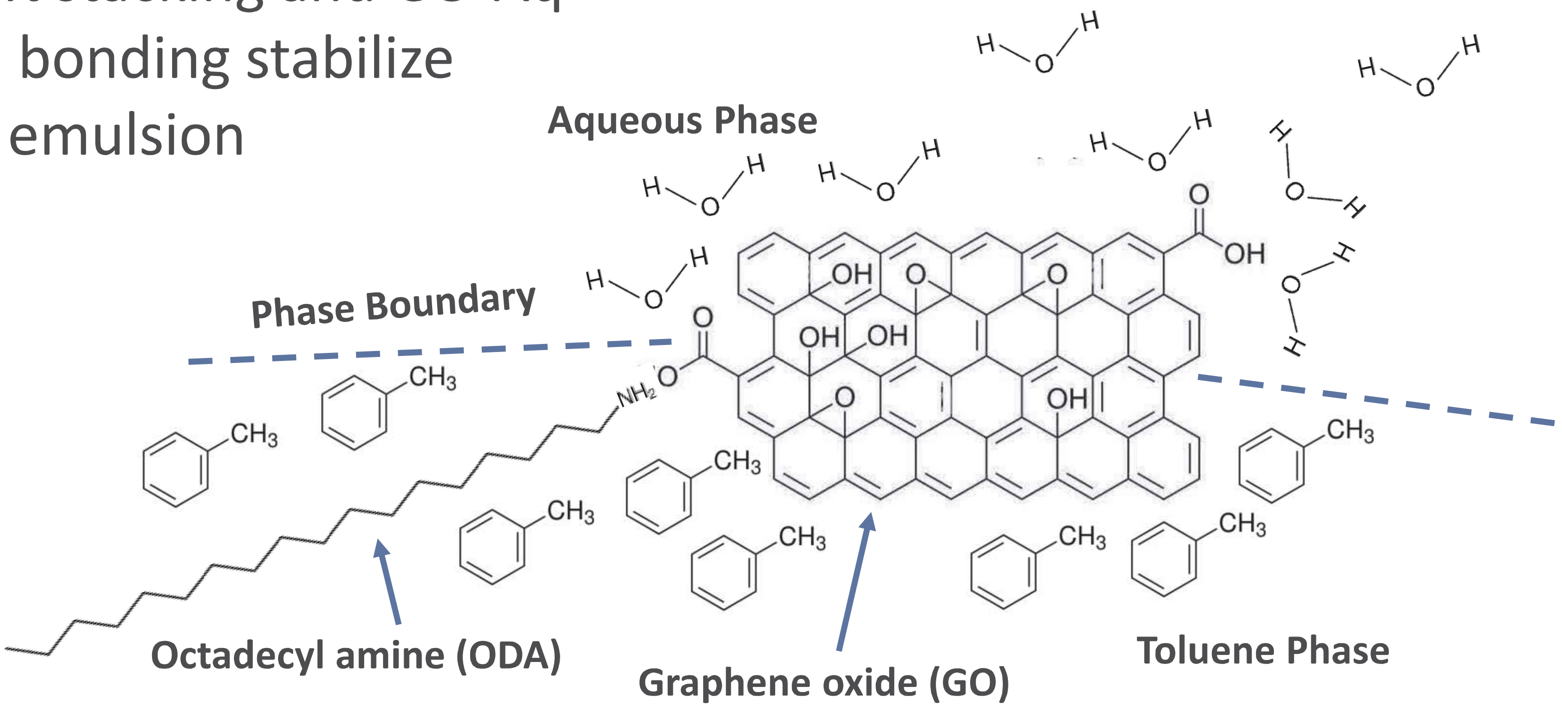


- Emulsified graphene oxide (GO) inks
- High conductivity and porosity
- Low density and viscosity
- Open cell foam morphology

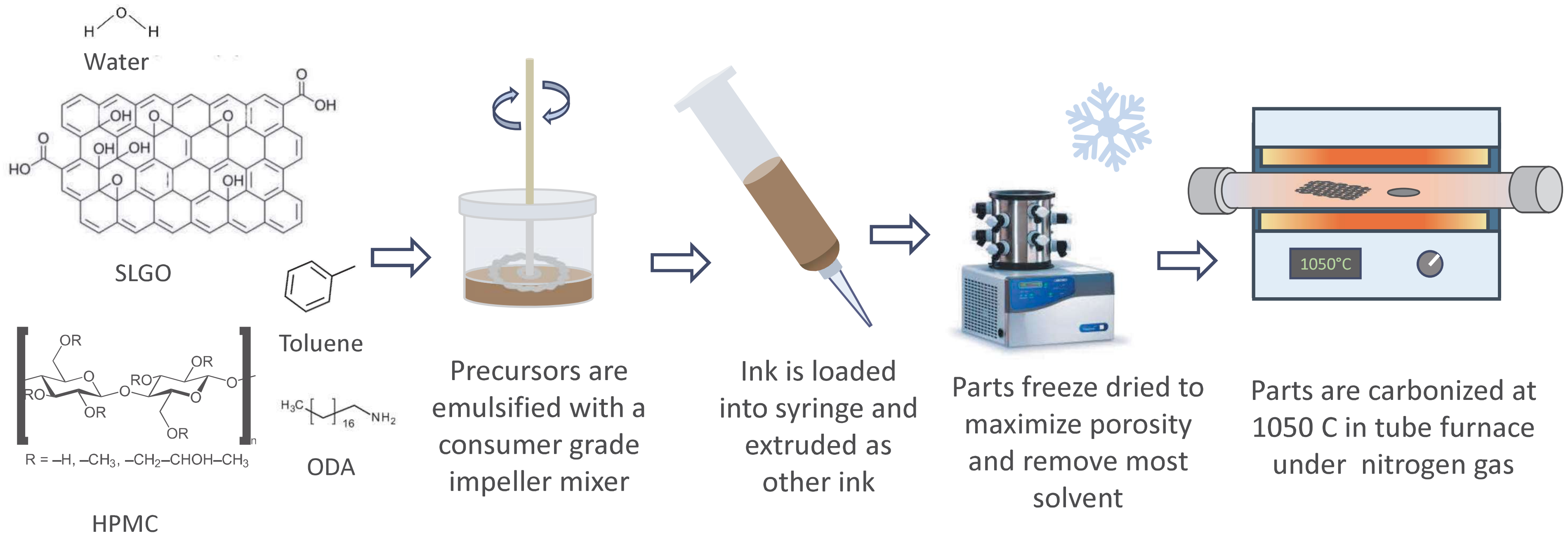
Lulu Li, Zhiming Deng, Mengjie Chen, Zhong-Zhen Yu, Thomas P. Russell, and Hao-Bin Zhang
Nano Letters **2023** *23* (1), 155-162
DOI: 10.1021/acs.nanolett.2c03821

GO Emulsion Formulation

- ODA functionalizes GO and both sit at phase boundary
- GO-Tol π-π stacking and GO-Aq hydrogen bonding stabilize Pickering emulsion



GO Emulsion Formulation



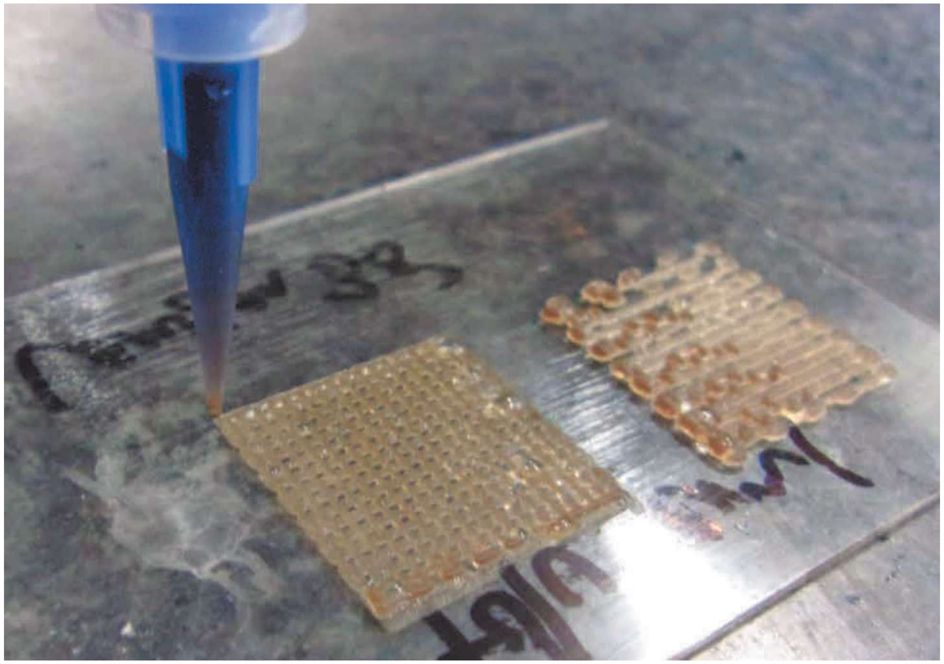
Precursors are emulsified with a consumer grade impeller mixer

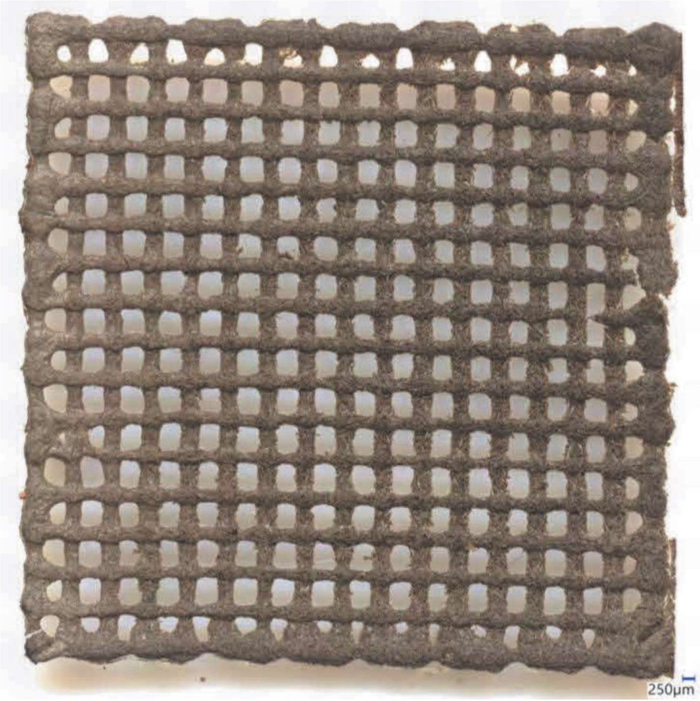
Ink is loaded into syringe and extruded as other ink

Parts freeze dried to maximize porosity and remove most solvent

Parts are carbonized at 1050 C in tube furnace under nitrogen gas

GO Emulsion Printing

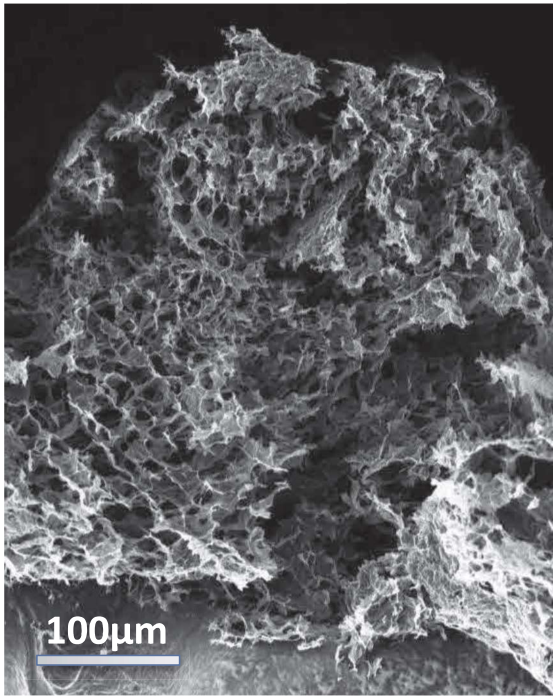


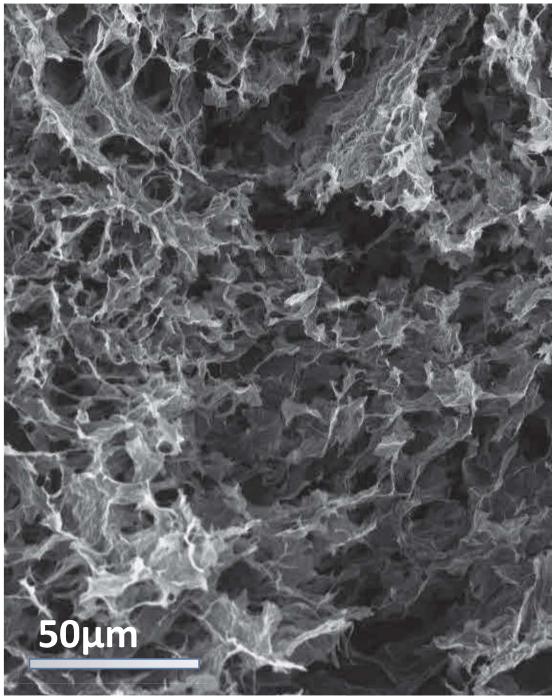


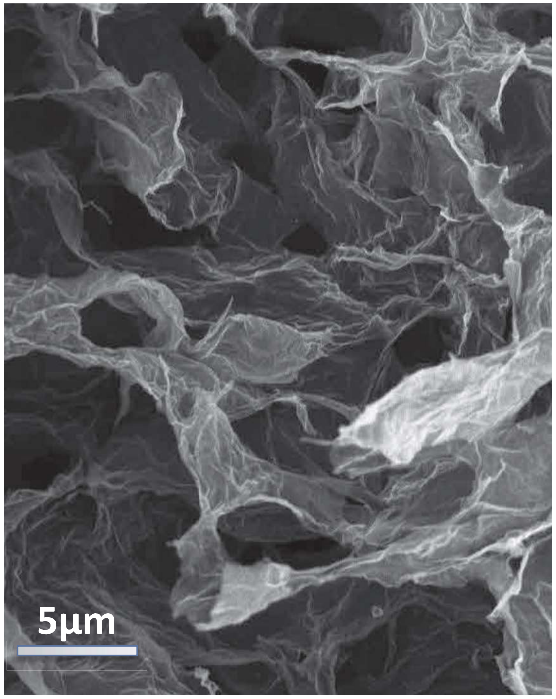
Initial emulsions were very soft and could barely print

Adding HPMC allowed better stiffness + printability, and still made good finished parts

SEM Images of GO Emulsion







- Progressively zoomed in SEMs show open pore structure of printed and carbonized emulsion part.

Conclusions

- PEDOT:PSS inks were made more conductive by addition of GNP
- GO Emulsion inks were made more printable with addition of HPMC

Thank You Everyone!

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