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Multifunctional, 3D-Printable Inks for Energy Products (Energy Inks)

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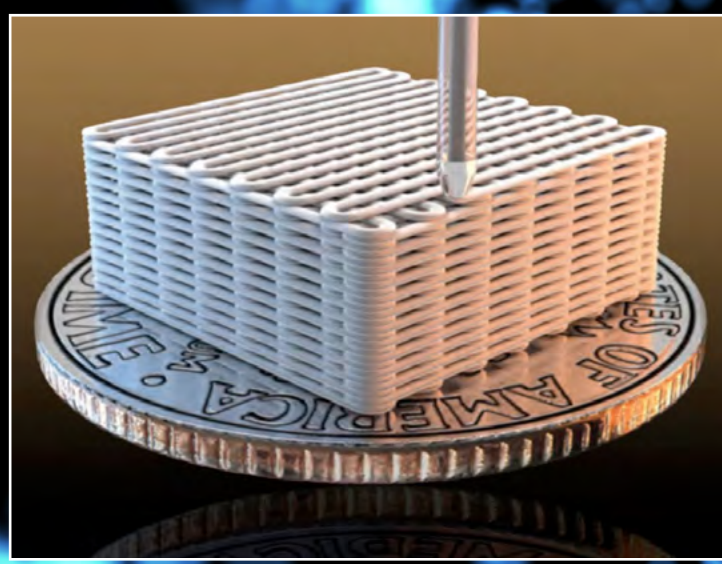
R&D 100
Award Entry



LLNL-MI-834683

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Multifunctional, 3D-Printable Inks for Energy Products (Energy Inks)

1. PRODUCT/SERVICES CATEGORIES

A. Title

Multifunctional, 3D-Printable Inks for Energy Products (Energy Inks)

B. Product Category

Mechanical/Materials

2. R&D 100 PRODUCT/SERVICE DETAILS

A. Primary submitting organization

Lawrence Livermore National Laboratory

B. Co-developing organizations

MilliporeSigma, a division of Merck KGaA, Darmstadt, Germany

C. Product brand name

MilliporeSigma 3D Printable Graphene Oxide Ink

MilliporeSigma 3D Printable Yttria-stabilized Zirconium(IV) Oxide Ink

MilliporeSigma 3D Printable Ultra-High Temperature Boron Carbide Ink

D. Product Introduction

This product was introduced to the market between January 1, 2021, and March 31, 2022. This product is not subject to regulatory approval.

E. Price in U.S. Dollars

3D Printable Graphene Oxide Ink: $125.00 (10 ml)
https://www.sigmaaldrich.com/US/en/product/aldrich/916579?context=product

3D Printable Yttria-stabilized Zirconium(IV) Oxide Ink: $62.40 (10 g)
https://www.sigmaaldrich.com/US/en/product/aldrich/918571

3D Printable Ultra-High Temperature Boron Carbide Ink: $60.00 (30 g)
https://www.sigmaaldrich.com/US/en/product/aldrich/921912

F. Short description

Energy Inks meet 3D printing material flow conditions while optimizing functional properties of the extruded material, requirements difficult to obtain simultaneously. Such functional inks enable the design of customizable, easily integrated components, and, therefore, next-generation high-performance energy devices including those not possible to produce using current methods.

G. Type of institution represented

Government or independent lab/institute

H. Submitter's relationship to product

Product developer

I. Photos

Attached inline

J. Video

1. https://www.linkedin.com/feed/update/urn:li:activity:6912041717592375296?updateEntityUrn=urn%3Ali%3Afs_feedUpdate%3A%28V2%2Curn%3Ali%3Aactivity%3A6912041717592375296%29 3D Printable Graphene Oxide Ink

2. https://youtu.be/csLiOo5ykis 3D Printable Yttria-stabilized Zirconium(IV) Oxide Ink

3. https://youtu.be/j7uCFI04CBk 3D Printable Ultra-High Temperature Boron Carbide Ink

3. PRODUCT/SERVICE DESCRIPTION

A. What does the product or technology do?

Imagine being able to select a printer feedstock and print a functioning battery. The capability to 3D print functioning devices has been made possible with Energy Inks, 3D-printing feedstock inks developed by Lawrence Livermore National Laboratory (LLNL).

3D printing with polymers allowed a newer and more efficient method of prototyping. Now Energy Inks, which have functional properties, are optimized to enable next-generation, high-performance, 3D-printed devices for energy storage, catalysis, filtration, sensors, and more. Devices once thought too complex and costly for commercial distribution can now be 3D-printed faster, at a lower cost, and exhibit higher performance with Energy Inks. With the world's growing demand for electronics, energy storage devices, and clean energy technologies, Energy Inks play a significant role in meeting a critical need.

Although 3D-printing offers control and reproducibility to efficiently create optimized solid-state electrode architectures on a large scale, the inks required to make functioning components have not been available until now. Energy Inks not only enable the printing of battery and supercapacitor components but optimize their functional properties. The ability to economically produce any form factor will revolutionize this world of products.

Obtaining the flow conditions needed for 3D printing while maintaining the functional properties of the extruded material is a craft that is not straightforward. The result, developed by LLNL, revolutionizes the kind of energy-sector products that can be produced through the additive manufacturing technology of direct ink writing (DIW), enabling novel designs that can meet a growing, global need in revolutionary ways.

Additive manufacturing with Energy Inks has been demonstrated to maintain the intrinsic capacitance for carbon materials as well as the hardness and extreme temperature performance of ultra-high-temperature ceramics. In tests published by the Energy Inks team (Chandrasekaran, et. al., 2020, *Materials and Design*), electrodes printed with Energy Inks surpass competitive compositions on all energy-storage-related parameters.

Flexible graphene, inorganic, and carbon-based Energy Inks enable 3D printing of devices for applications such as supercapacitors, lithium-ion batteries, hydrogen fuel cells, catalysts, filtration devices, heat exchangers, sensors, and others. Further, the technology offers the opportunity to tailor energy storage and conversion devices by, for example, increasing strength-to-weight ratios for improved electric vehicle performance, performing in harsh environments, and meeting other performance characteristics, thereby optimizing a range of energy applications.

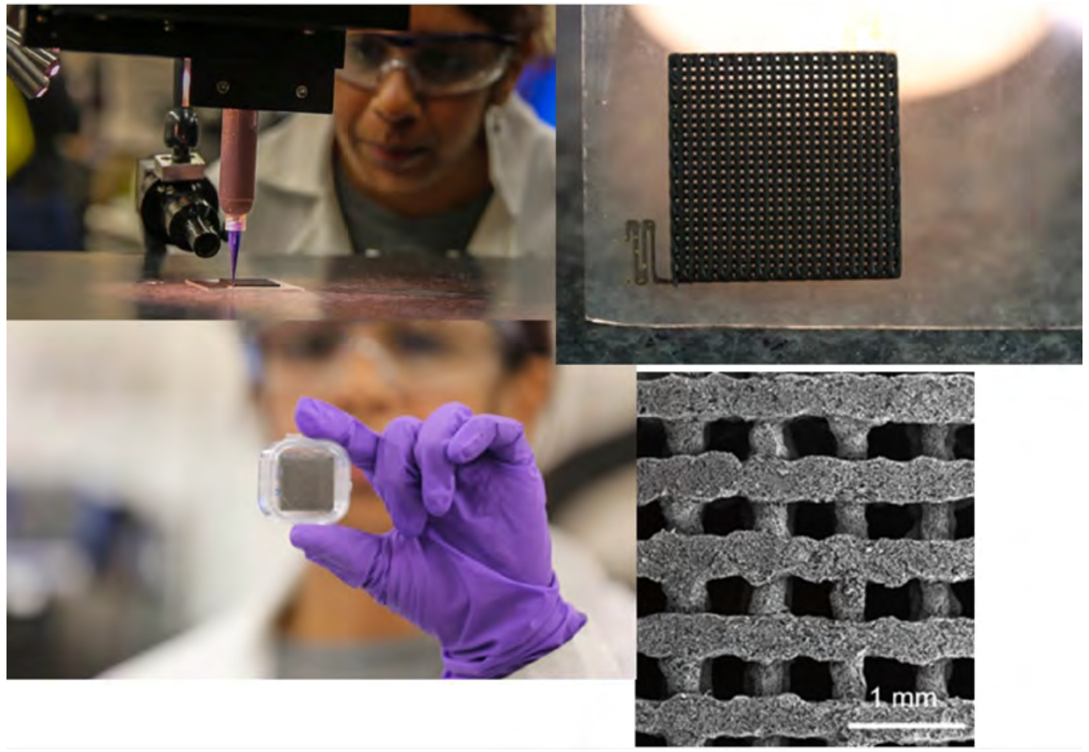

Figure 1: Lawrence Livermore/MilliporeSigma Energy Inks maintain the functional properties of materials used to fabricate energy storage devices in an ink with the necessary viscosity and drying characteristics for effective 3D printing.

The collaboration between LLNL and MilliporeSigma makes these Energy Inks available to researchers at companies and universities worldwide to pursue their own projects. In 2021, LLNL and global chemical and materials supplier MilliporeSigma introduced Energy Inks to users for applications in consumer electronics, transportation, and medical devices.

The MilliporeSigma product line includes:

- 3D Printable Graphene Oxide Ink
- Yttria-stabilized Zirconium(IV) Oxide Ink, and
- Ultra-High Temperature Boron Carbide Ink.

Following are the characteristics and applications of each product:

3D Printable Graphene Oxide (GO) Ink

Tailored for DIW for complex-shaped parts with 200 μm resolution

Applications: batteries, supercapacitors, electrocatalysis

- Based on graphene oxide (GO) nanosheets (4 wt.%)
- Stable dispersion of GO, leading to long shelf life
- High viscosity (100-210 Pa.s (25 °C) @ 10 s^{-1} shear rate)

3D-printable graphene-based ink promises fast charge rates, increased cycle-life, and improved gravimetric capacitance for next generation energy storage devices. In a collaboration with University of California, Santa Cruz, LLNL researchers 3D-printing a graphene aerogel electrode demonstrated, for the first time, a simultaneous increase in both energy and power densities due to improved electrolyte infiltration and ion diffusion, compared to earlier iterations. The electrode achieved record-breaking performance, overcoming conventional tradeoffs for supercapacitors with the highest areal storage capacitance (electric charge storage per unit area) recorded to date, as published in Yao, et al., 2020, *Advanced Materials*.

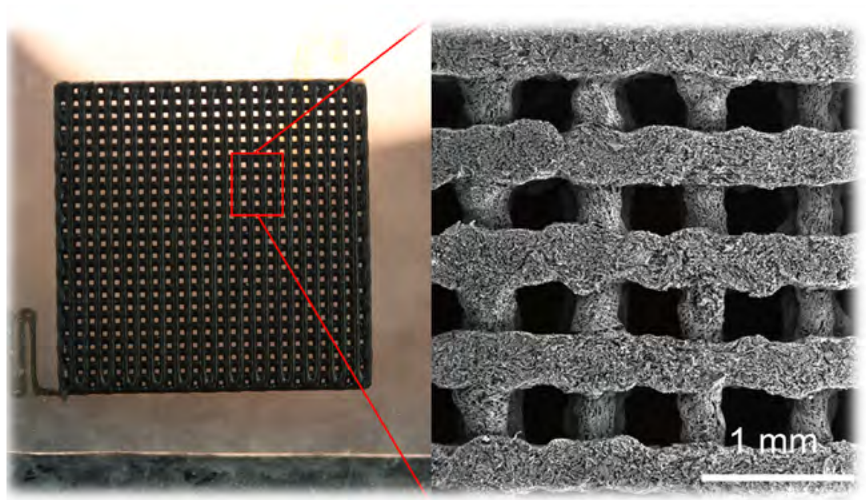

Figure 2: 3D Printable Graphene Oxide Ink

3D Printable Yttria Stabilized Zirconia (YSZ) Ink

Suitable for DIW or tuned for stereolithography for complex-shaped parts with 250 μm, 400 μm resolution

Applications: membranes, catalysis, reactors

- Based on yttria stabilized zirconia (YSZ) nanoparticles (70 wt%)
- Stable dispersion of YSZ, leading to long shelf life
- High viscosity (2-25 Pa.s @100s^{-1} shear rate)

These ceramic feedstock inks remain chemically and mechanically robust in extreme temperatures and high pH, pointing to applications in energy storage/conversion, separations, and sensor devices. Porous ceramics are ideal for use in filtration, catalysis, and thermal insulation due to high surface area and tunable porosity and can be used to retrofit in current power plant designs.

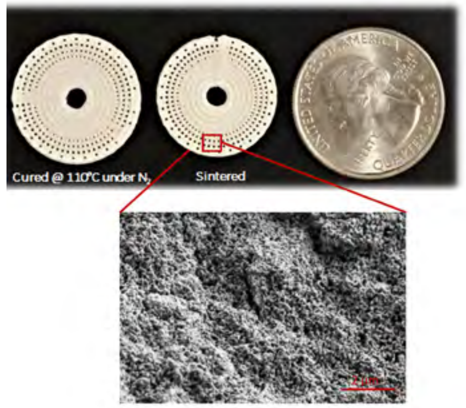

Figure 3: 3D Printable Yttria Stabilized Zirconia Ink

3D Printable Ultra-High Temperature B_4C Ink

Suitable for various DIW printing technologies for complex-shaped parts with 400 μm resolution

Applications: heat exchanges, high wear components, components in extreme temperature environments

- Based on boron carbide (B_4C) microparticles (64.4 wt.% equivalent to 50 vol.%)
- Stable dispersion of B_4C, leading to long shelf life
- High viscosity (10-100 Pa.s @100s^{-1} shear rate)

This lightweight, super-hard, ultra-high-temperature ceramic material can be used for components subjected to extreme temperatures and high-wear environments, such as nuclear reactors, or for light-weight body armor.

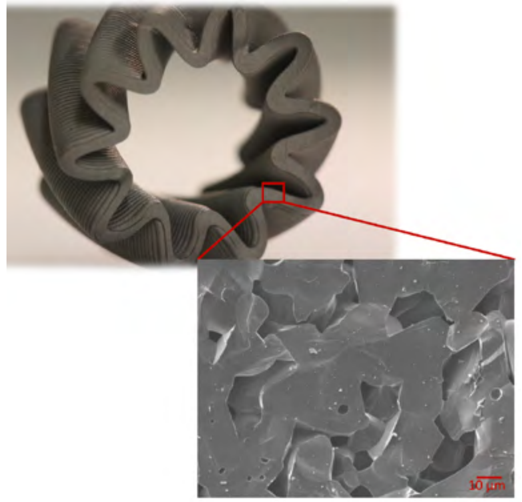

Figure 4: 3D Printable Ultra-High Temperature B_4C Ink

The technology also brings supercapacitors closer to the point of wide utilization. Supercapacitors have long been investigated for their potential energy storage capabilities. While recharging takes mere minutes and performance is preserved beyond thousands of charge cycles, supercapacitors' low storage capacity means they are rarely used in place of regular batteries.

However, recent research placing pseudocapacitive materials within a 3D-printed graphene aerogel scaffolding has shown that storage capacity can still be functionally increased, approaching that of conventional batteries. An impossible feat if relying only on traditional manufacturing methods, incorporating lightweight graphene aerogel promotes supercapacitors as a viable energy storage method that is particularly effective when recharge speed and overall weight are limiting factors, such as with long-range electric vehicles and perhaps even all-electric airliners.

Experiments with the Energy Inks technology demonstrated the highest areal storage capacitance to date at 3231 mF/cm^2, maintaining a capacitance of 2195 mF/cm^2 at a high current density of 100 mA/cm^2, even at a high mass loading of 12.8 mg/ cm^2. These results promise the development of thinner and lighter energy storage devices that use fewer assembly parts and yet remain high performing.

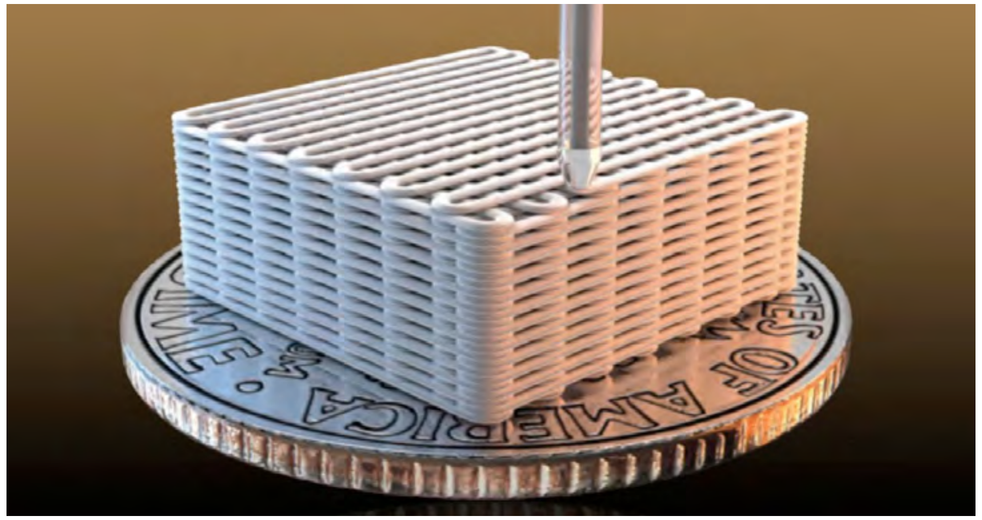

Figure 5: Lawrence Livermore's precision, direct ink writing process can print complex architectures used in energy storage devices and other energy-related devices.

B. How does the product operate?

Direct ink writing (DIW) – also known as "robocasting" – is a popular additive manufacturing method that robotically extrudes continuous "ink" filaments through a micronozzle to form a 3D object layer-by-layer on a three-axis motion stage. The technique is commonly used to create product prototypes from polymers, although it has been adapted for use in a diverse range of extruded materials.

LLNL researchers adapted DIW technology to precisely deposit graphene oxide inks in a pre-defined tool path to form 3D structures. When characterized for compression and capacitance performance, researchers observed that the printed architectures exhibited better performance than conventionally manufactured counterparts.

Additive manufacturing with Energy Inks has been demonstrated to maintain the intrinsic capacitance for carbon materials as well as the hardness and extreme temperature performance of ultra-high-temperature ceramics. The LLNL/ MilliporeSigma team has demonstrated the range of possibilities for customized devices from batteries, catalysts, and fuel cells to heat exchangers and desalination devices, among others, that could be 3D-printed using Energy Inks.

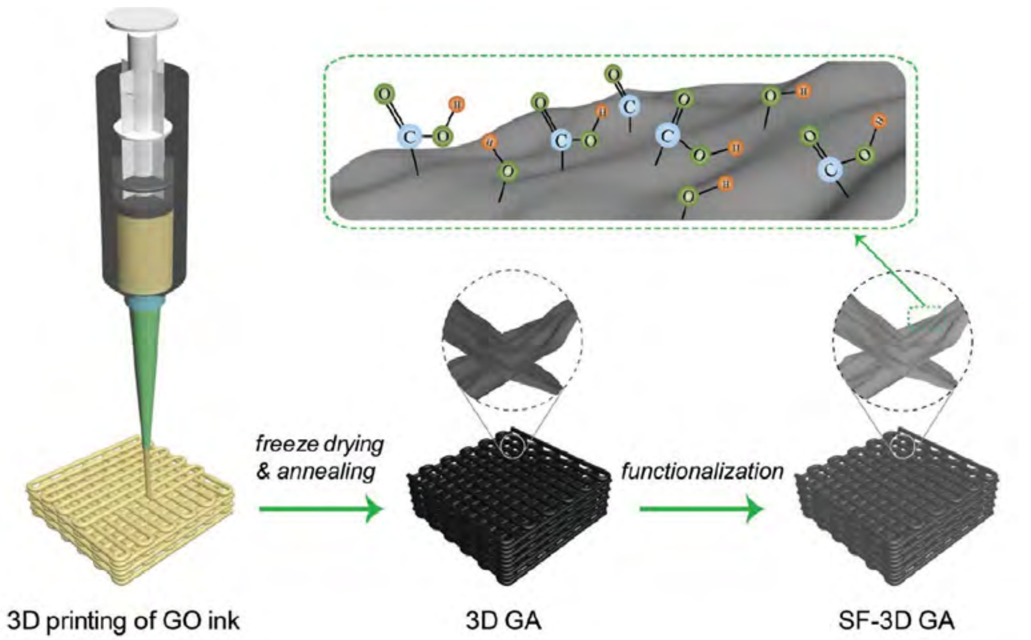

Figure 6: Steps for 3D printing of graphene oxide ink

With Energy Inks, a breadth of functional ink substances can be used to 3D print electrodes for energy storage devices such as supercapacitors, lithium-ion batteries, and other battery configurations. The collaborative LLNL and MilliporeSigma focus on additive manufacturing has enabled Energy Inks to maintain both the intrinsic capacitance for carbon materials as well as the hardness and extreme temperature performance of ultra-high-temperature ceramics.

Structures printed with Energy Inks were found to exhibit better compression and capacitance performance than those using conventional counterparts. Printed aerogel electrodes are a primary target for the materials' application. The electrode printing process begins by extruding the graphene oxide ink into a lattice structure. The structure is then freeze-dried and annealed to convert the graphene oxide aerogels into pure graphene aerogels. Researchers at the University of California proceeded to electrochemically oxidize the aerogel to introduce surface functional groups. This surface-functionalized aerogel form was finally reduced in solution to improve electrical conductivity. Scanning electron microscopy (SEM) of the aerogel before and after surface functionalization indicated that the electrochemical oxidation process did not lead to any changes of the 3D-printed structure or structural relationships of the starting material.

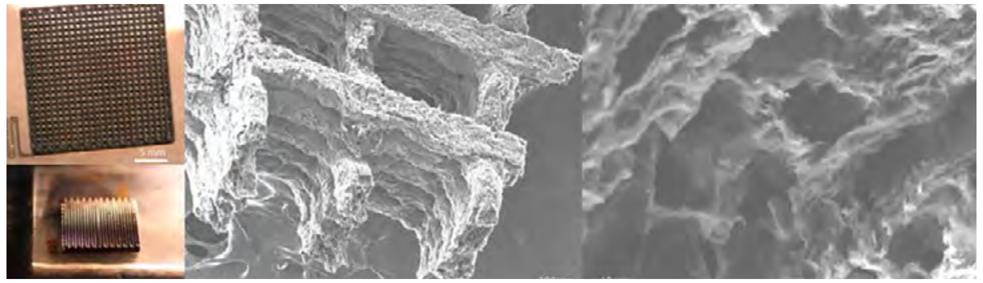

Figure 7: Digital (center) and SEM images (far right) of the printed graphene aerogel (far left) indicate the material's characteristic porous structure, demonstrating that functional characteristics were maintained through the 3D printing process.

C. Product Comparison

A major feature of Energy Inks is the ability to produce highly-customizable forms that can be easily integrated with other 3D printed components to create an optimized energy storage device. While these capabilities are not new in their own right—powder-based 3D printing and selective laser sintering have previously been used for similar purposes—Energy Inks excel over these alternative methods in ease of use, process efficiency, and the high level of precision offered by 3D printing. This manufacturing mode coupled with functional inks will make designs possible that were heretofore uneconomical.

Energy Inks compare favorably to traditional manufacturing and other printing approaches by offering ease of integration and device tailoring combined with faster manufacturing speed, low cost, low waste, and better-performing devices. When matched against traditional manufacturing of energy storage technologies, Energy Inks offer a more environmentally friendly approach because the 3D printing process reduces energy consumption and material waste.

While competitive manufacturing techniques such as powder-based 3D printing, selective laser sintering, ink jet printing, and traditional manufacturing offer tradeoffs in terms of customization, cost, and other factors, none combine the ease, efficiency, and high level of precision offered by 3D printing. Most importantly, compared to Energy Inks, other existing 3D-printable materials lack optimization for energy storage applications.

D. Comparison summary

Characteristics	Technologies: Energy Inks LLNL/Millipore Sigma	Powder-based 3D printing OR Selective Laser Sintering	Ink Jet Printing	Standard Manufacturing
Highly-tailorable forms	Yes	Yes	No	No
Ease of integration with other 3D-printed components	Yes	Yes	No	No
Cost	Low	High	High	Low
Micron-sized features	Yes	No	Yes	No
Wastage from machining or post-processing	No	Yes	No	Yes
Re-usability	Yes	Yes	Yes	No
Larger builds	Yes	Yes	No	Yes
Design flexibility	Yes (high)	Yes (high)	Yes (limited)	No

Table 1: Comparison of Energy Inks to Competitors

E. Limitations

Next steps seek to scale the product offerings, enabling a transition to large-scale manufacturing.

4. SUMMARY

Energy Inks, 3D-printing feedstock inks developed by Lawrence Livermore National Laboratory (LLNL) and introduced to the market in three formulations by partner MilliporeSigma, offer functional properties, enabling next-generation, high-performance, 3D-printed devices for energy storage, catalysis, filtration, sensors, and more. Further, with Energy Inks, these devices can be 3D-printed faster, at a lower cost, and exhibit higher performance than competitive technologies. Energy Inks not only enable the printing of battery and supercapacitor components but optimize their functional properties. Making use of the design flexibility afforded by direct ink writing (DIW), customizable storage components can be produced, lowering the costs associated with production. For commercial products, the technology relieves cost and time limitations to speed up marketplace introduction. With the growing global demand for electronics, energy storage devices, and clean energy technologies, Energy Inks play a significant role in meeting a critical need.

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7. SUPPORT LETTERS

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