Batteries: Direct-write Microbatteries for Microelectronic Devices

Mesoscale electrochemical charge-storage devices (e.g., batteries and ultracapacitors) will likely serve as the sole power source or a component of a hybrid power source for new microelectronic systems (Swider-Lyons *et al*. 2002, Harb *et al*. 2002). Batteries are usually discharged over several hours and are used to supply energy (watt-hours). Ultracapacitors discharge over seconds to minutes, and are therefore good sources of power (watts). Batteries and ultracapacitors have a minimal heat signature, generate no noise, and have no moving parts, so they will cause little interference to microelectronic systems.

Every battery and ultracapacitor cell has seven major components: (i) positive electrode, (ii) negative electrode, (iii) separator, (iv) electrolyte, (v) current collectors, (vi) packaging, and (vii) interconnects to an electronic load. The cell chemistry and geometry determines its energy, power, and discharge properties (Vincent and Scrosati 1997).

In microelectronic systems, it is not effective to use traditional surface-mounted batteries fabricated using standard manufacturing methods, because the packaging and interconnects would dominate the size and weight of the power source. Size and weight can be conserved by writing microbatteries directly into microelectronic circuits so that the electronic substrate serves as part of the battery packaging and the interconnect lengths are reduced. Direct write by laser forward-transfer is an ideal process for fabricating microbatteries, because it is compatible with the commercially available polymers, metal oxides, and metals used in batteries (Piqué *et al*. 1999, Piqué and Chrisey 2002). Processing is carried out in ambient conditions, making feasible the deposition of corrosive electrolytes and hydrous materials. The CAD/CAM features allow the rapid prototyping necessary for device optimization. Additional laser micromachining can be used to tailor the size and interfaces of the microbatteries to achieve a high-performance laser-engineered power source. Laser forward transfer has been used to fabricate conformal, mesoscale passive electronic components, including metal interconnects, multilayer capacitors, inductors, and resistors.

1. Laser Direct-write Process for Microbattery Fabrication

The laser forward-transfer of a positive electrode of a lithium-ion battery is shown schematically in Fig. 1. An ink formulation for the positive electrode (including a lithium metal oxide, carbon, and a polymeric binder) is mixed with a liquid vehicle that either serves as or is compatible with the battery electrolyte. A $\sim$10 μm thick film of the ink is spread onto an ultraviolet (UV)-transparent glass plate which is mounted in front of a pulsed UV-laser (355 nm) over an appropriate substrate. The laser forward transfers the solid and liquid of the ink from the glass onto the substrate. The amount of material transferred is a function of the laser fluence, laser spot size (10–100 μm diameter), and ink thickness. The substrate moves on a computer-controlled

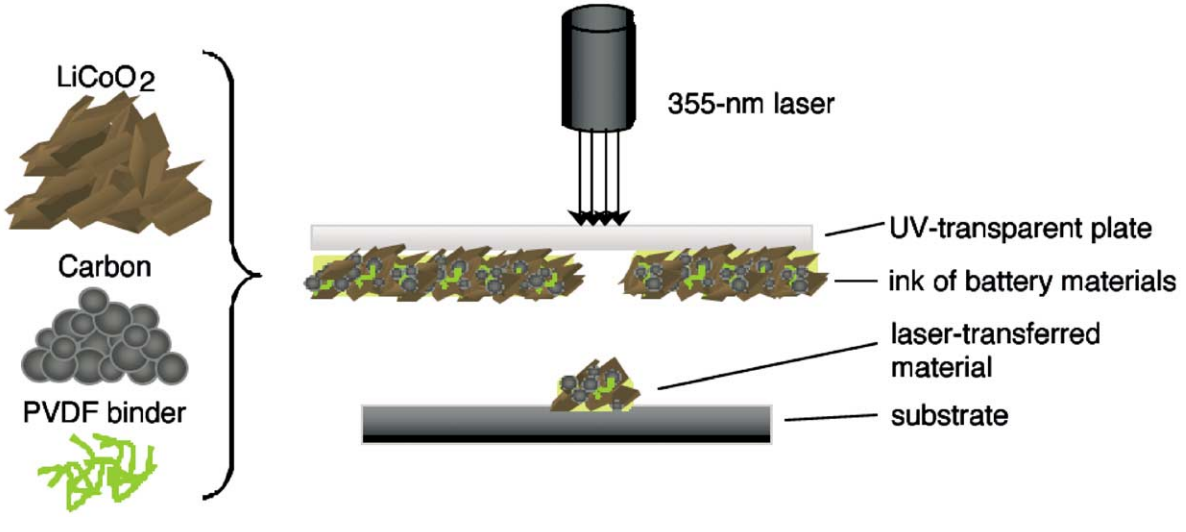

Figure 1
Schematic diagram illustrating the laser direct-write process for the transfer of a $LiCoO_2$ battery cathode.

translation stage underneath the laser during transfer. Subsequent laser micromachining is used to modify the design of the transferred material or the substrate for systems integration. The transferred material can be post-processed using conventional heating methods or laser annealing.

2. Batteries

2.1 Direct-write Lithium-ion Microbatteries

The laser-transferred electrodes of a lithium-ion microbattery are shown in Fig. 2(a). The positive electrode is transferred onto aluminum foil from an ink of $LiCoO_2$, carbon, polyvinylidene fluoride (PVDF), and 1-methyl 2-pyrrolidone. The negative electrode is transferred on copper foil from an ink of carbon and 1-methyl 2-pyrrolidone. After vacuum drying, the positive electrode cycles reversibly in a 1 M $LiClO_4$ propylene carbonate electrolyte and has similar voltammetric features to that of a stenciled electrode. A 600 μg, 3 mm × 3 mm × 40 μm $LiCoO_2$ electrode discharged at a 12-hour rate yields a capacity of 100 mWh g^{-1}, which is only 10% below the theoretical capacity of the material. Microscopy and x-ray diffraction confirm that the laser-transferred $LiCoO_2$ retains its morphology and is not preferably oriented during laser transfer.

A battery can be assembled in a dry environment by adding a lithium electrolyte to the electrodes, and then pressing the electrodes together. In Fig. 2(b), the assembly is surface mounted with silicone epoxy to a diode circuit to create a low-volume, low-weight power source. If the interconnects were deposited with laser direct write, the weight of the battery would be further reduced.

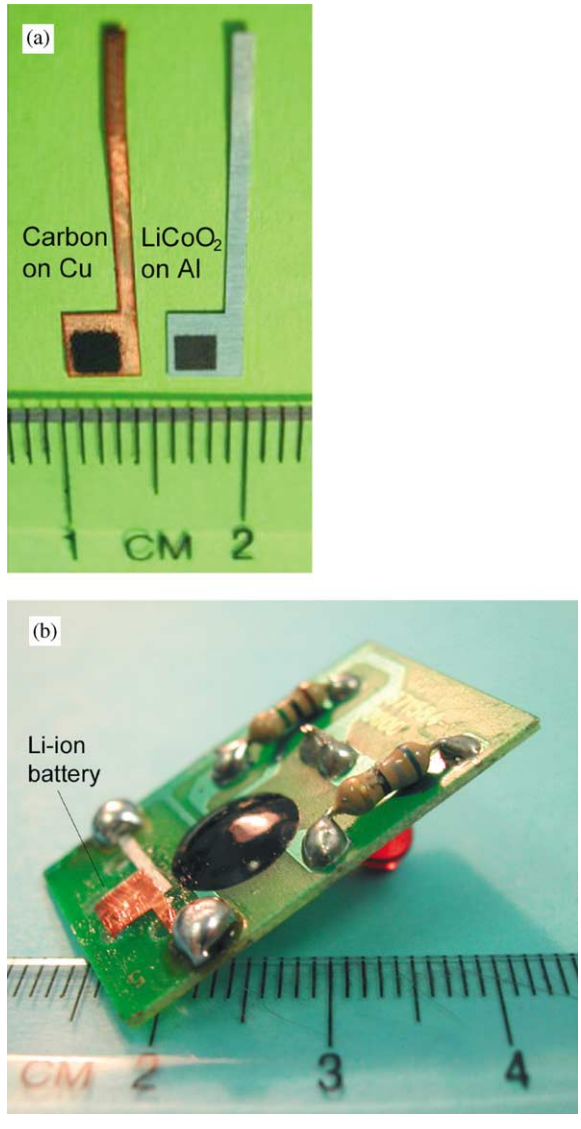

Figure 2
(a) Lithium-ion battery electrodes transferred with laser direct write; (b) prototype lithium-ion battery surface mounted in a diode circuit.

2.2 Direct-write Hydrous RuO_2 Micro-ultracapacitors

Planar micro-ultracapacitors of hydrous RuO_2 have positive and negative electrodes with identical compositions (Swider-Lyons *et al.* 2000, Arnold *et al.* 2002). A cell is fabricated by depositing hydrous RuO_2 on a gold-coated glass substrate and then micromachining a 20 μm line through the hydrous RuO_2 and gold. The hydrous RuO_2 is transferred from a sulfuric-acid ink and packaged under a Nafion film. The laser-processed hydrous RuO_2 devices have comparable electrochemical characteristics to those prepared with traditional processing (Burke 2000), because the porosity of the metal oxide is retained and the hydrous RuO_2 remains hydrated. Cells which weigh ~80 μg and are 1 mm × 2 mm × 15 μm in volume yield specific energies of 1100 mW g^{-1} and 10 mWh g^{-1} when discharged between 10 μA and 1 mA (Arnold *et al.* 2002). The cells can be discharged up to 50 mA without damage. Two cells linked in parallel or in series yield doubled capacities and potentials, respectively, indicating that the laser-machined lines allow uniform discharge of the cells.

2.3 Direct-write Alkaline Microbatteries

A stacked alkaline microbattery has been fabricated by laser depositing a 2 mm × 3 mm^2 pad of an hydrous electrolytic-MnO_2 composite (including carbon, a binder, and KOH) in contact with a

gold-coated glass substrate. The MnO_2 pad is covered with a 4 mm $\times$ 5 mm^2 pad of ethyl cellulose and laser-transferred 2 mm $\times$ 3 mm^2 pad of zinc. These alkaline microbatteries have the expected cell voltage of 1.5 V and can power a digital watch for over 10 min (Piqué *et al*. 2001, Swider-Lyons *et al*. 2002).

3. Concluding Remarks

Laser direct write is an ideal method for making electrochemical power sources, including microbatteries and micro-ultracapacitors. Lithium-ion and alkaline batteries plus hydrous RuO_2 ultracapacitors have been fabricated by direct write from commercially available materials. The laser transfer and processing has no apparent adverse effect on the materials properties. Challenges remain in the development of direct-write electrochemical power sources, particularly with the current collectors, packaging, and interconnects needed to fully integrate the ultracapacitors and microbatteries into microelectronic circuits.

Once the full systems for the microbatteries and micro-ultracapacitors are completed, the two power sources may be combined into a hybrid power source to supply high energy and high power to a microelectronics system. The battery design can be configured to tailor the battery discharge profile to match the energy and power demands of an electronic device. Ultimately, the energy-storage devices may be integrated with energy-harvesting systems, for instance on the back of a solar cell, to economize the system weight and volume and create a high energy-density micropower source system for long-term autonomous operation of microelectronic devices (Swider-Lyons *et al*. 2002, Harb *et al*. 2002).

Acknowledgement

This research is sponsored by the Office of Naval Research. CBA and RCW are post-doctoral fellows with the National Research Council and American Association for Engineering Education, respectively.

See also: Batteries: Glassy Electrolytes; Batteries, Rechargeable

Bibliography

Arnold C B, Wartena R C, Swider-Lyons K E, Piqué A 2002 Direct-write planar micro-ultracapacitors by laser engineering. *J. Electrochem Soc*. in press

Burke A 2000 Ultracapacitors: why, how, and where is the technology? *J. Power Sources* **91**, 37–50

Harb J N, LaFollette R M, Selfridge R H, Howell L L 2002 Microbatteries for self-sustained hybrid micropower supplies. *J. Power Sources* **104**, 46–51

Piqué A, Chrisey D B (eds.) 2002 *Direct-write Technologies for Rapid Prototyping Applications*. Academic Press, San Diego, CA

Piqué A, Chrisey D B, Auyeung R C Y, Fitz-Gerald J, Wu H D, McGill R A, Lakeou S, Wu P K, Nguyen V, Duignan M 1999 A novel laser process for direct writing of electronic and sensor materials. *Appl. Phys. A*. **69** (Suppl.), S279–84

Piqué A, Swider-Lyons K E, Weir, D W, Love C T, Modi R 2001 Laser direct writing of microbatteries for integrated power electronics. In: *Laser Applications in Microelectronic and Optoelectronic Manufacturing VI*, SPIE Proc. SPIE, Bellingham, WA, Vol. **4274**, pp. 316–22

Swider-Lyons K E, Piqué A, Arnold C B, Wartena R C 2002 Direct-write microbatteries for next-generation microelectronic devices. In: *Electroactive Polymers and Rapid Prototyping*. MRS, Warrendale, PA, Vol. 698.

Swider-Lyons K E, Weir D W, Love C T, Modi R, Sutto T, Piqué A, Chrisey D B 2000 Direct-write microbatteries as integrated power sources for microelecronic devices. In: *Power Sources for the New Millennium*. Electrochemical Society, Pennington, NJ, Vol. 2002-22, pp. 272–6

Vincent C A, Scrosati B 1997 *Modern Batteries*: *An Introduction to Electrochemical Power Sources*, 2nd edn. Wiley, New York

Zheng JP, Cygan PJ, Jow TR 1995 Hydrous ruthenium oxide as an electrode material for electrochemical capacitors. *J. Electrochem. Soc*. **142**, 2699–703

K. E. Swider-Lyons, A. Piqué, C. B. Arnold and R. C. Wartena

Encyclopedia of Materials: Science and Technology
ISBN: 0-08-043152-6
pp. 1–3