

Laser Scribing of High-Performance and Flexible Graphene-Based Electrochemical Capacitors

Maher F. El-Kady, *et al.*
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Materials and Methods

SOM Text

Figs. S1 to S7

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Laser Scribing of High-Performance and Flexible Graphene-Based Electrochemical Capacitors

Maher F. El-Kady,^{1,2} Veronica Strong,¹ Sergey Dubin,¹ Richard B. Kaner^{1,3*}

Although electrochemical capacitors (ECs), also known as supercapacitors or ultracapacitors, charge and discharge faster than batteries, they are still limited by low energy densities and slow rate capabilities. We used a standard LightScribe DVD optical drive to do the direct laser reduction of graphite oxide films to graphene. The produced films are mechanically robust, show high electrical conductivity (1738 siemens per meter) and specific surface area (1520 square meters per gram), and can thus be used directly as EC electrodes without the need for binders or current collectors, as is the case for conventional ECs. Devices made with these electrodes exhibit ultrahigh energy density values in different electrolytes while maintaining the high power density and excellent cycle stability of ECs. Moreover, these ECs maintain excellent electrochemical attributes under high mechanical stress and thus hold promise for high-power, flexible electronics.

Batteries and electrochemical capacitors (ECs) stand at opposite ends of the spectrum in terms of their power and energy densities (1). Batteries store energy through electrochemical reactions and can exhibit high energy densities (on the order of 20 to 150 Wh/kg), whereas ECs, which store charge in electrochemical double layers (EDLs), can only achieve values of 4 to 5 Wh/kg (2–4). However, because ion flow is faster than redox reactions ECs can deliver much higher power densities. ECs are also generally maintenance free and display a longer shelf and cycle life, so they are often favored in many electronic applications (2–4).

An EC that combines the power performance of capacitors with the high energy density of batteries would represent a major advance in energy storage technology (5, 6), but this requires an electrode with higher and more accessible surface area than that of conventional EC electrodes while maintaining high conductivity. Graphene-based materials are attractive in this regard be-

cause of their mechanical and electrical properties as well as exceptionally high surface area. Recently, the intrinsic capacitance of single-layer graphene was reported to be ~21 μ F/cm²; this value now sets the upper limit for EDL capacitance for all carbon-based materials (7). Thus, ECs based on graphene materials could, in principle, achieve an EDL capacitance as high as ~550 F/g if their entire surface area could be used.

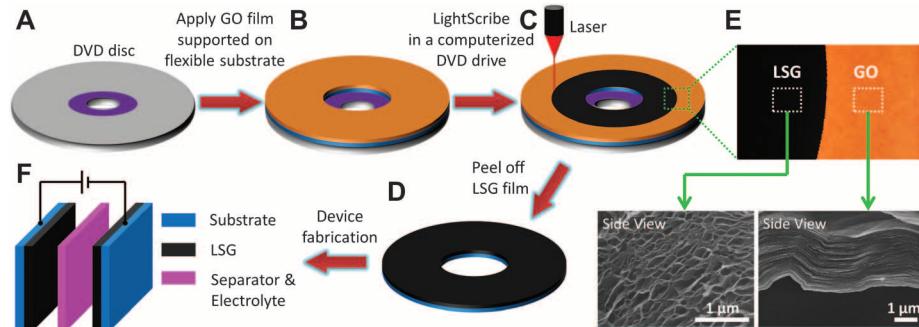


Fig. 1. Schematic illustration of the fabrication of laser-scribed graphene-based electrochemical capacitors. (A to D) A GO film supported on a flexible substrate is placed on top of a LightScribe-enabled DVD media disc, and a computer image is then laser-irradiated on the GO film in a computerized LightScribe DVD drive. (E) As shown in the photograph, the GO film changes from golden brown color to black as it reduced to laser-scribed graphene. The low-power infrared laser changes the stacked GO sheets immediately into well-exfoliated few-layered LSG film, as shown in the cross-sectional SEM images. (F) A symmetric EC is constructed from two identical LSG electrodes, ion-porous separator, and electrolyte.

¹Department of Chemistry and Biochemistry and California NanoSystems Institute, University of California, Los Angeles (UCLA), Los Angeles, CA 90095, USA. ²Department of Chemistry, Faculty of Science, Cairo University, Giza 12613, Egypt. ³Department of Materials Science and Engineering, UCLA, Los Angeles, CA 90095, USA.

*To whom correspondence should be sent. E-mail: kaner@chem.ucla.edu

production of mechanically robust graphene electrodes with large thickness (~10 μm or higher) and high surface-to-volume ratio in a binderfree process would result in high power and high energy density ECs (5).

Here, we present a strategy for the production of graphene-based ECs through a simple all-solid-state approach that avoids the restacking of graphene sheets. The process is schematically illustrated in Fig. 1. Initially, a thin film of GO dispersed in water was drop-cast onto a flexible substrate (fig. S1). Irradiation of the film with an infrared laser inside an inexpensive commercially available LightScribe CD/DVD optical drive, as discussed in (17), reduces the GO to laser-scribed graphene (LSG), as indicated by the change in film color from golden brown to black. Analysis of cross sections of the film with scanning electron microscopy showed that the initially stacked GO sheets were converted into well-exfoliated LSG sheets through laser irradiation (Fig. 1E and fig. S2). The resulting LSG films showed excellent conductivity (1738 S/m) as opposed to 10 to 100 S/m for activated carbons, the state-of-the-art material used in commercial devices (18). Additionally, LSG shows excellent mechanical flexibility with only ~1% change in the electrical resistance of the film after 1000 bending cycles [supporting online material (SOM) section 2 and fig. S3]. Thus, LSG can be directly used as EC

electrodes without the need for any additional binders or conductive additives. More importantly, these properties allow LSG to act as both the active material and current collector in the EC. The combination of both functions in a single layer leads to a simplified and lightweight architecture. Thus, a device can be readily made by sandwiching an ion porous separator [Celgard 3501 (Celgard, Charlotte, NC)] between two identical LSG electrodes. The devices are super-thin with a total thickness of <100 μm , making them potentially useful in microdevice applications (fig. S4) (19). Other devices can be made by putting LSG on porous substrates such as a nitrocellulose membrane or photocopy paper or on conductive aluminum foil, which is often used in commercial devices (figs. S1 and S7). Therefore, LSG electrochemical capacitors (LSG-ECs) can be readily made into different designs, including stacked and spirally wound structures to target different applications.

The LSG electrodes we have fabricated satisfy the critical features for high-performance ECs. First, the large and accessible specific surface area of the LSG (1520 m^2/g compared with 1000 to 2000 m^2/g for a typical activated carbon material) results in a sizeable charge storage capacity and accounts for the high areal and volumetric stack capacitances observed. Second, the LightScribe laser causes the simultaneous re-

duction and exfoliation of GO sheets and produces an open network of LSG (Fig. 1). This structure prevents the agglomeration of graphene sheets, which has been a major barrier in achieving the full potential of graphene-based ECs. The network structure of LSG has open pores, which helps facilitate the electrolyte accessibility to the electrode surfaces. This offers an opportunity to optimize the ionic diffusion in LSG electrodes, which is crucial for charging the EDL, and generates high-power ECs. Last, LSG possesses excellent electronic conductivity, which is another key factor for achieving high power. These three properties taken together and optimized could, in theory, produce landmark performances in EC electrodes. Working with these properties, three-dimensional composite electrodes have been successfully used to make batteries with relatively high energy density and fast charge/discharge rates (20). Although activated carbons can provide high surface area, the difficulty of controlling their pore structure and pore size distribution has so far limited the energy densities and rate capabilities of commercial ECs (21).

In order to demonstrate the superior performance of LSG electrodes for electrochemical energy storage, we assembled symmetric LSG-ECs using polyethylene terephthalate (PET) as a thin flexible substrate and an aqueous electrolyte of 1.0 M H_3PO_4 . The EC performance was

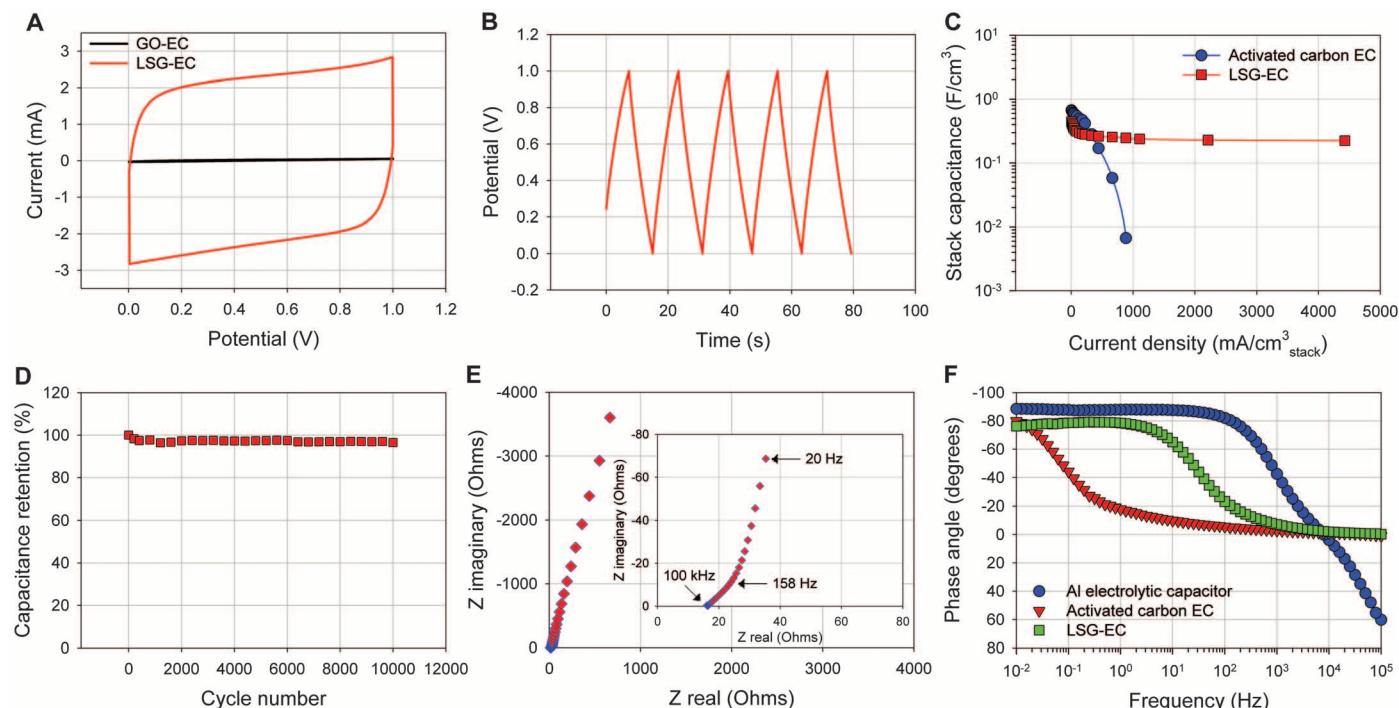


Fig. 2. Evaluation of the performance of an LSG electrochemical capacitor in aqueous 1.0 M H_3PO_4 solution. (A) Cyclic voltammometry of LSG- and GO-ECs at a scan rate of 1000 mV/s. A rectangular CV shape is observed for the LSG-EC, indicating an efficient double-layer formation. (B) Galvanostatic charge/discharge (CC) curves of an LSG-EC measured at a high current density of 10 A/g_{LSG/electrode}. (C) The volumetric stack capacitance of an LSG-EC is calculated from the CC curves at different charge/discharge current densities. Data obtained from a commercial activated carbon EC are shown for comparison.

As can be seen, an LSG-EC can sustain ultrahigh current density operation, indicating the potential for ultrahigh-power delivery. (D) The LSG-EC shows excellent cyclic stability and retains >96.5% of its initial response after 10,000 cycles. (E) Complex plane plot of the impedance of a LSG-EC, with a magnification for the high-frequency region in the inset. (F) Impedance phase angle versus frequency for a LSG-EC and a commercial activated carbon EC. The -45° phase angle occurs at ~30 Hz for the LSG-EC and at ~0.1 Hz with the commercial EC.

analyzed through both cyclic voltammetry (CV) and galvanostatic charge/discharge (CC) experiments, as shown in Fig. 2. In comparison with GO, the LSG-EC shows an enhanced electrochemical performance with a nearly rectangular CV shape at a scan rate of 1000 mV/s, which is indicative of nearly ideal capacitive behavior (Fig. 2A) even though no metal current collector, binders, or electroactive additives were used, as is the case in commercial ECs. Additionally, the LSG-EC is robust enough to be charged and discharged over a wide range of scan rates (100 to 10,000 mV/s) and still maintain its nearly ideal rectangular CV shape (figs. S5 to S7). Figure 2B shows the nearly triangular shape of the CC curves obtained at a high current density of 10 A/g of LSG per electrode (abbreviated 10 A/g_{LSG/electrode}). This is indicative of the formation of an efficient EDL and fast ion transport within the LSG electrodes. In addition, these CC curves show only a small voltage drop of 0.018 V at the start of the discharge curve, indicating a device with a low equivalent series resistance (ESR). We measured the specific capacitance from CC curves over a wide range of charge/discharge current densities. Here, the areal and volumetric capacitance of the stack (this includes the flexible substrate,

the current collector, the active material, and the separator) were calculated and compared with a commercial activated-carbon EC (AC-EC) tested under the same dynamic conditions. Although the AC-EC shows a slightly higher volumetric capacitance at low charge/discharge rates, its capacitance falls off quickly at higher rates, whereas the LSG-EC continues to provide high capacitance even when operated at very high rates (Fig. 2C and fig. S8). In addition, the areal capacitance of the LSG-EC was calculated to be 3.67 mF/cm² [and 4.04 mF/cm² in 1.0 M H₂SO₄ (figs. S5 to S7)] at 1 A/g_{LSG/electrode}. The device also shows a very high rate capability while still maintaining a capacitance of more than 1.84 mF/cm², even when the EC is operated at an ultrafast charge/discharge rate of 1000 A/g_{LSG/electrode}. This is comparable with values reported in the literature for micro-devices and thin-film ECs at much lower current charge/discharge rates (0.4 to 2 mF/cm²) (5, 13). As is shown in fig. S6, these ECs can be efficiently charged/discharged on the 0.1-s time scale. Additionally, the LSG-EC retained 96.5% of its initial capacitance after 10,000 cycles (Fig. 2D).

Electrochemical impedance spectroscopy (EIS) confirmed the fast ion transport within the LSG electrodes. A complex plan plot of the impedance

data of the LSG-EC is shown in Fig. 2E with an expanded view provided in the inset. The device displays a pure capacitive behavior, even at high frequencies of up to ~158 Hz. The series resistance of the device is estimated to be ~16 ohms. This value can be attributed to the contact resistance of the device with the external circuit that could be reduced by using current collectors. The dependence of the phase angle on the frequency for the LSG-EC, AC-EC, and an aluminum electrolytic capacitor is shown in Fig. 2F. For frequencies up to 10 Hz, the phase angle of the LSG-EC is close to -90°, which suggests that the device functionality is close to that of an ideal capacitor. The characteristic frequency f_0 for a phase angle of -45° is 30 Hz for the LSG-EC. This frequency marks the point at which the resistive and capacitive impedances are equal (22). The corresponding time constant τ_0 ($=1/f_0$) equals 33 ms compared with 10 s for the conventional AC-EC and 1 ms for the aluminum electrolytic capacitor. This rapid frequency response of the LSG-EC can be accounted for by the large and accessible surface area of the LSG, whose exposed flat sheets enhance the ion transport rate in the device (23). This is consistent with results reported recently for an EC made from vertically

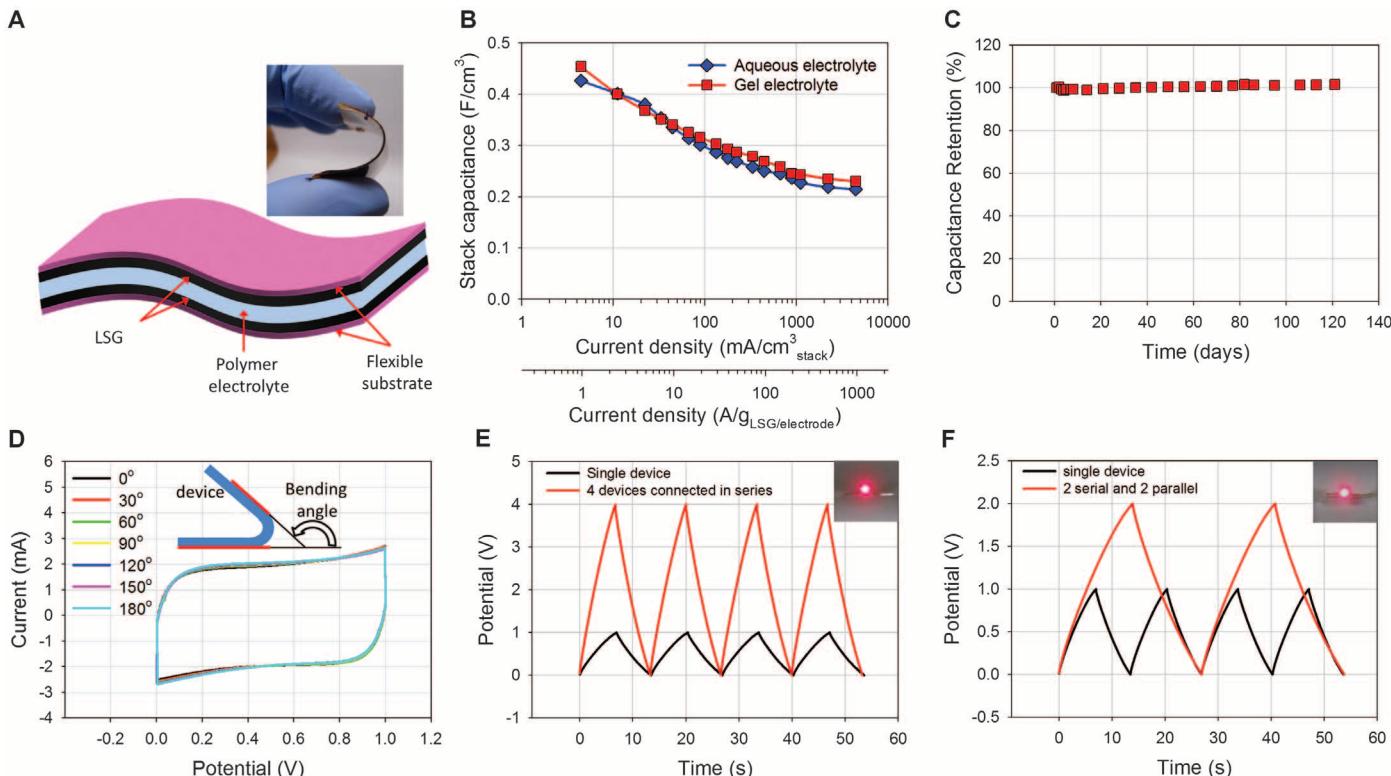


Fig. 3. Design and fabrication of a flexible, all-solid-state LSG electrochemical capacitor. **(A)** A schematic diagram of the all-solid-state LSG-EC illustrates that the gelled electrolyte can serve as both the electrolyte and separator. (Inset) A digital photograph showing the flexibility of the device. **(B)** A comparison between performances of LSG-EC using gelled versus aqueous electrolytes. Both devices show similar capacitance values at all the tested charge/discharge current densities. **(C)** A shelf-life test shows excellent stability for over 4 months without any obvious degradation. **(D)** Bending the device

has almost no effect on its performance, as seen in these CVs collected at a scan rate of 1000 mV/s. Galvanostatic charge/discharge curves for four tandem ECs connected **(E)** in series, and **(F)** in a combination of series and parallel. A single device is shown for comparison. Both the tandem devices and the single device were operated at the same constant current charge/discharge. The serial connection extends the output voltage to 4 V (versus 1 V for a single device), whereas the output voltage and current can both be doubled with the serial-parallel connection. (Insets) The glow of an LED when powered by tandem LSG-ECs.

oriented graphene nanosheets grown directly on metal current collectors (24–26) and carbon nanotube electrodes made with an electrophoretic deposition technique (27, 28).

The future development of multifunctional flexible electronics such as roll-up displays, photovoltaic cells, and even wearable devices presents new challenges for designing and fabricating lightweight, flexible energy storage devices (29). Commercially available ECs consist of a separator sandwiched between two electrodes with liquid electrolyte, which is then either spirally wound and packaged into a cylindrical container or stacked into a button cell (3). Unfortunately, these device architectures not only suffer from the possible harmful leakage of electrolytes, but their design makes it difficult to use them for practical flexible electronics. We replaced the liquid electrolyte with poly(vinyl alcohol) (PVA)-H₃PO₄ polymer gelled electrolyte, which also acts as the separator (Fig. 3A, device structure). This electrolyte reduced the device thickness and weight compared with phosphoric acid and simplified the fabrication process because it does not require any special packaging materials. As demonstrated in Fig. 3B, at any given charge/discharge rate the specific capacitance values for the all-solid-state device were comparable with those obtained with

an aqueous electrolyte. The high-rate performance of this device can be accounted for by the porous structure of the LSG electrodes, which can effectively absorb the gelled electrolyte and act as an electrolyte reservoir to facilitate ion transport and minimize the diffusion distance to the interior surfaces (30). Another key factor is that LSG electrodes are binderfree—thus, enabling a reduction in interfacial resistance and enhancing the electrochemical reaction rate. The device performance was completely stable over 4 months of testing (Fig. 3C). As with the aqueous LSG-EC, the flexible all-solid-state LSG-EC maintains its excellent cycling stability: >97% of the initial capacitance was maintained even after 10,000 cycles (fig. S10).

In order to evaluate under real conditions the potential of this all-solid-state LSG-EC for flexible energy storage, a device was placed under constant mechanical stress and its performance analyzed. The CV performance of this device when tested under different bending conditions is shown in Fig. 3D. The bending had almost no effect on the capacitive behavior; it can be bent arbitrarily without degrading performance. Moreover, the stability of the device was tested for more than 1000 cycles while in the bent state, with only ~5% change in the device capacitance (fig. S11). This performance durability can be

attributed to the high mechanical flexibility of the electrodes along with the interpenetrating network structure between the LSG electrodes and the gelled electrolyte. The electrolyte solidifies during the device assembly and acts like a glue that holds all the device components together, improving the mechanical integrity and increasing its cycle life even when tested under extreme bending conditions. Because this remarkable performance has yet to be realized in commercial devices, these ECs may be ideal for next-generation flexible, portable electronics.

Portable equipment often require cells packaged either in series, in parallel, or in combinations of the two in order to meet energy and power requirements. For example, laptop batteries commonly have four 3.6-V lithium ion cells connected in series to achieve a voltage of 14.4 V, and two in parallel to increase the capacity from 2400 mAh to 4800 mAh (31). Thus, it would be of interest to develop an EC that could exhibit control over the operating voltage and current by using tandem serial and parallel assemblies with minimal energy losses. The performances of a set of tandem LSG-EC were evaluated by assembling four devices both in series and in parallel configurations. Compared with a single EC, which operates at 1.0 V, the tandem series ECs exhibited a 4.0-V charge/discharge voltage window (Fig. 3E). In the parallel assembly, the output current increased by a factor of 4, and thus the discharge time was four times that of a single device when operated at the same current density (figs. S12 to S14). As expected, when the four ECs were combined two in series and two in parallel, both the output voltage and the runtime (capacitive current) increased by a factor of 2 under the same charge/discharge current (Fig. 3F). As with the single devices, the tandem devices show essentially perfect triangular CC curves with a minuscule voltage drop, which again indicates excellent capacitive properties with minimal internal resistance. Thus, when used in tandem, the LSG-ECs undergo minimal energy losses. As a demonstration, a tandem EC's ability to light a red light-emitting diode (LED) that operates at a minimum voltage of 2 V is shown in the Fig. 3, E and F, insets.

We also examined an organic electrolyte, which would allow the operation of the devices at higher voltages, thus achieving higher energy densities. In this case, tetraethylammonium tetrafluoroborate dissolved in acetonitrile was used because this is the most common organic electrolyte used in commercial devices (3). As shown in Fig. 4, the LSG-EC again exhibits enhanced performance and rate capabilities when compared with the commercial AC-EC; this is consistent with the data acquired in the aqueous and gelled electrolytes. Furthermore, the LSG-EC can be operated over a wider voltage window of 3 V. This EC offers a specific capacitance of up to 4.82 mF/cm² (265 F/g_{LSG/electrode}) and retains a capacitance of 2.07 mF/cm² when operated at the ultrahigh current density of 1000 A/g_{LSG/electrode} (fig. S15).

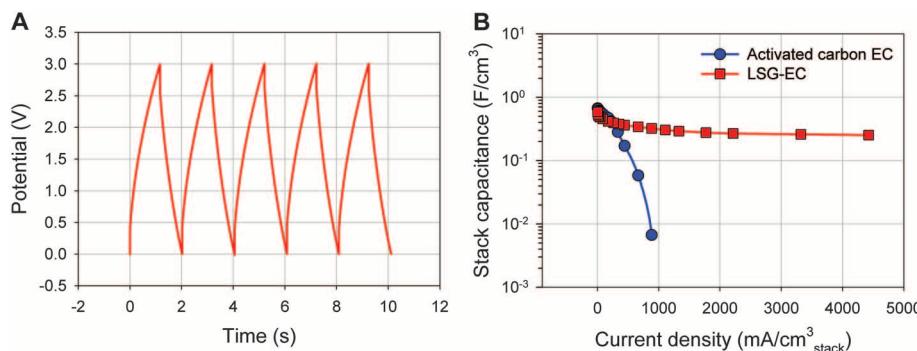
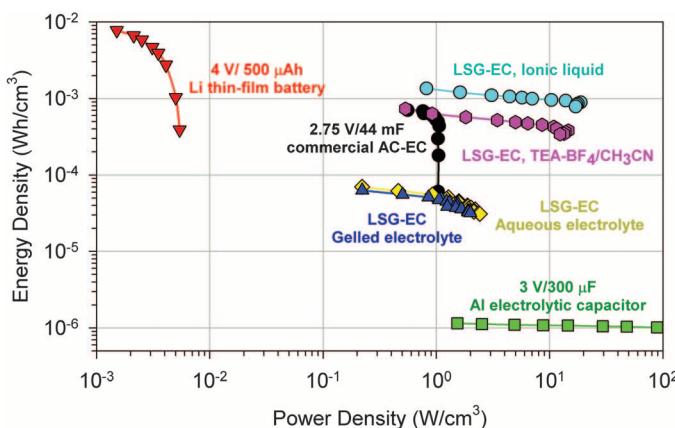


Fig. 4. The performance of a LSG electrochemical capacitor using an organic electrolyte of 1.0 M tetraethylammonium tetrafluoroborate dissolved in acetonitrile. (A) Galvanostatic charge/discharge curves of the device when operated at an ultrahigh current density of 250 A/g_{LSG/electrode}, showing near symmetric triangular shapes. (B) Stack capacitance values calculated from galvanostatic curves as a function of the applied charge/discharge current density showing the high rate performance possible with a LSG-EC versus that of an activated carbon EC.

Fig. 5. Energy and power densities of LSG-ECs compared with commercially available AC-EC, aluminum electrolytic capacitors, and a lithium thin-film battery. The LSG-ECs exhibit electrochemical energy storage with both ultrahigh power and energy densities. [The data for the Li thin-film battery are reproduced from (5) with permission from Nature Publishing Group]



Recently, room-temperature ionic liquids have been intensively studied as an attractive alternative to conventional electrolytes for ECs because of their high ion density, good thermal stability, and nonvolatility, as well as their wider potential window when compared with organic electrolytes (14, 32). We fabricated an LSG-EC using the ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF₄) that exhibited a specific capacitance as high as 5.02 mF/cm² (276 F/g_{LSG/electrode}) and at a wider potential window of 4 V (fig. S16). A prototype LSG-EC was made and encapsulated in the EMIMBF₄ electrolyte, charged at a constant potential of 3.5 V, and used to light up a red LED for ~24 min (movie S1).

In order to demonstrate the overall performance of the LSG-ECs using various electrolytes, a Ragone plot is shown in Fig. 5 comparing the performance of LSG-ECs with different energy storage devices designed for high-power microelectronics. This includes a commercial 2.75 V/44 mF AC-EC and a 500-μAh thin-film lithium battery and a 3 V/300 μF aluminum electrolytic capacitor, all tested under the same dynamic conditions (SOM section 9). The plot shows the volumetric energy density and power density of the stack for all the devices tested. The LSG-EC can exhibit energy densities of up to 1.36 mWh/cm³, a value that is approximately two times higher than that of the AC-EC. Additionally, LSG-ECs can deliver a power density of ~20 W/cm³, which is 20 times higher than that of

the AC-EC and three-orders of magnitude higher than that of the 500-μAh thin-film lithium battery. Although the electrolytic capacitor delivers ultrahigh power, it has an energy density that is three orders of magnitude lower than the LSG-EC. Because of the simplicity of the device architecture and the availability of the graphite oxide precursor, which is already manufactured on the ton scale, these LSG-ECs hold promise for commercial applications.

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threading dislocations extending to the surface (5). From a practical point of view, threading dislocations are most undesirable, because they may penetrate active device regions far away from a dislocated interface. Numerous methods have been more or less successful in reducing threading dislocation densities (6–18).

Equally fundamental problems arise for applications requiring thick layers, such as high-brightness light-emitting diodes, power transistors, or multiple-junction solar cells. Different thermal expansion coefficients of layers and substrates then often cause layer cracking (19) and wafer bowing (20), prohibiting further wafer processing or causing device failure. Regarding these effects, frequently dwarfing the dislocation problem in practical importance, no satisfactory solution has been found to date.

In the quest for a viable path toward the monolithic integration of an x-ray imaging detector onto

Scaling Hetero-Epitaxy from Layers to Three-Dimensional Crystals

Claudio V. Falub,^{1*} Hans von Känel,¹ Fabio Isa,² Roberto Bergamaschini,³ Anna Marzegalli,³ Daniel Chrastina,² Giovanni Isella,² Elisabeth Müller,⁴ Philippe Niedermann,⁵ Leo Miglio³

Quantum structures made from epitaxial semiconductor layers have revolutionized our understanding of low-dimensional systems and are used for ultrafast transistors, semiconductor lasers, and detectors. Strain induced by different lattice parameters and thermal properties offers additional degrees of freedom for tailoring materials, but often at the expense of dislocation generation, wafer bowing, and cracks. We eliminated these drawbacks by fast, low-temperature epitaxial growth of Ge and SiGe crystals onto micrometer-scale tall pillars etched into Si(001) substrates. Faceted crystals were shown to be strain- and defect-free by x-ray diffraction, electron microscopy, and defect etching. They formed space-filling arrays up to tens of micrometers in height by a mechanism of self-limited lateral growth. The mechanism is explained by reduced surface diffusion and flux shielding by nearest-neighbor crystals.

Quantum structures based on epitaxially grown semiconductor layers are a playground for studying electron transport and optical properties, especially at low temperatures, where electron mobilities have reached values above 30 million cm²/V·s (1). The discovery of fundamental phenomena such as the fractional quantum Hall effect (2) can be traced to the perfection of epitaxial heterostructures. Although progress has been faster for lattice-matched systems, the additional degree of freedom for band

structure engineering offered by strain has become increasingly attractive. Nowadays, most state-of-the art microprocessors exploit strained Si (3).

The strain introduced by growing a single-crystalline layer of one material on a second crystal differing in lattice parameter can persist only up to a certain critical thickness (4, 5). Beyond that thickness, segments of misfit dislocations form at the interface, gradually relieving the misfit strain as growth proceeds. Misfit dislocation segments are always accompanied by

¹Laboratory for Solid State Physics, ETH Zürich, Schafmattstrasse 16, CH-8093 Zürich, Switzerland. ²L-NESS, Department of Physics, Politecnico di Milano, via Anzani 42, I-22100 Como, Italy.

³L-NESS, Department of Materials Science, Università di Milano-Bicocca, via Cozzi 53, I-20126 Milano, Italy. ⁴Electron Microscopy Center, ETH Zürich, Schafmattstrasse 16, CH-8093 Zürich, Switzerland. ⁵Centre Suisse d'Electronique et Microtechnique, Jaquet-Droz 1, CH-2002 Neuchâtel, Switzerland.

*To whom correspondence should be addressed. E-mail: cfalub@phys.ethz.ch