3D-integrated all-solid-state batteries

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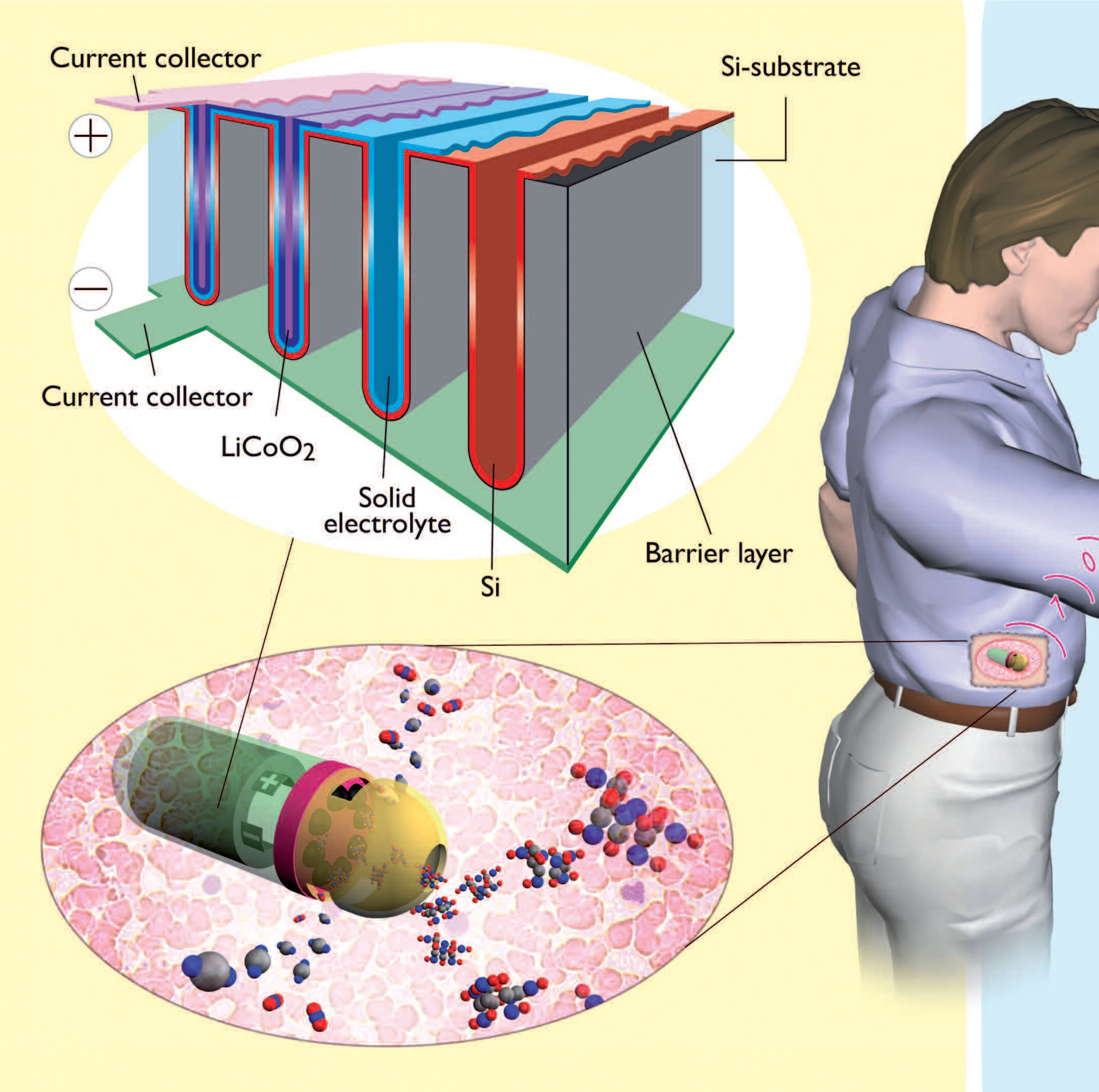
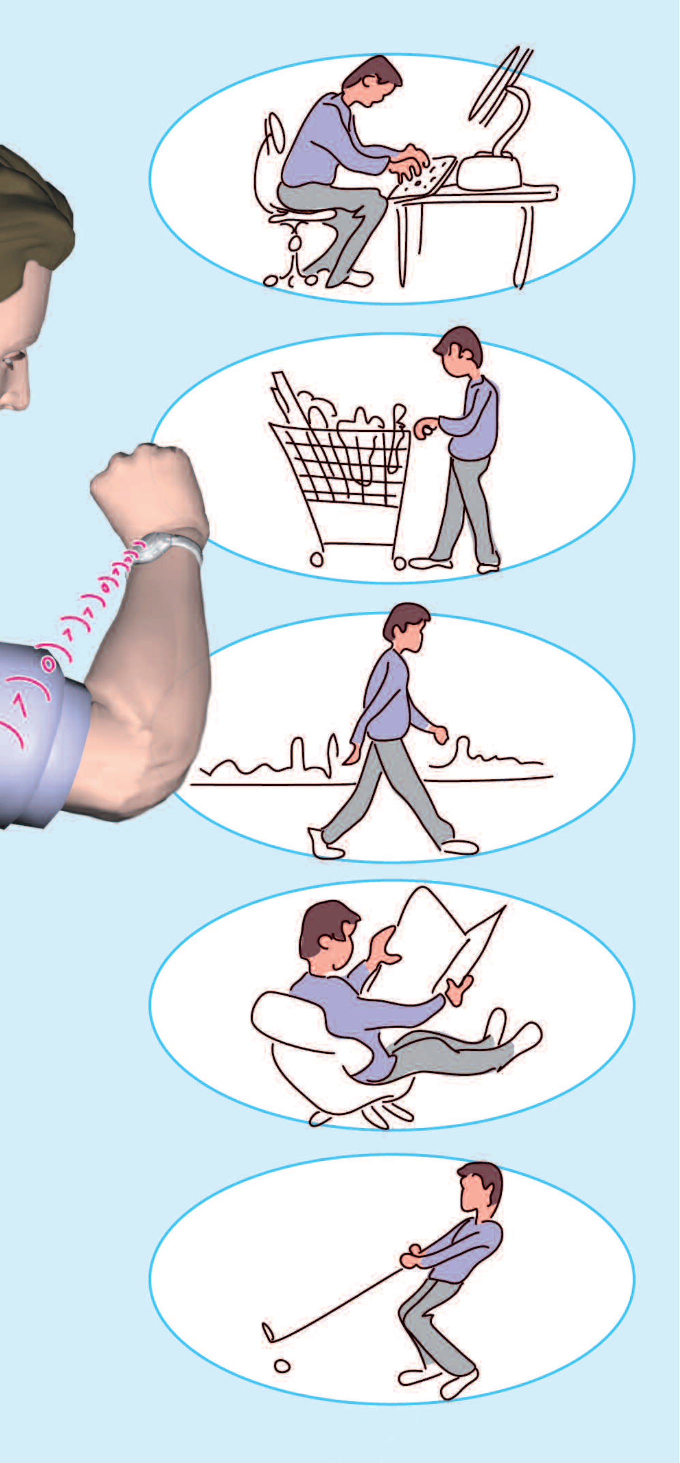


Article available at http://www.europhysicsnews.org or http://dx.doi.org/10.1051/epn/2011303

Electrification of our increasingly sophisticated society will proliferate rapidly during this century. A key element in the electricity supply chain is storage of electricity. Hydrogen and lithium have proved to be safe and reliable elements for electrical storage, yielding present-day rechargeable Nickel-Metal Hydride (NiMH) and lithium-ion batteries [1]. Underlying this development is basic research into thin film materials [2,3]. Innovative battery concepts include the 3D-integrated all-solid-state battery enabling future autonomous devices, large-scale storage and medical implants [1,4,5].



◀ Artist impression of the functioning of an implanted autonomous device, such as an electronic pill.

Small rechargeable batteries are of crucial importance to our "portable" society. Well-known examples are mobile phones, laptop computers and digital cameras. A strong tendency exists toward widening the range of application of rechargeable batteries extending to very large and very small appliances, see Figure 1.

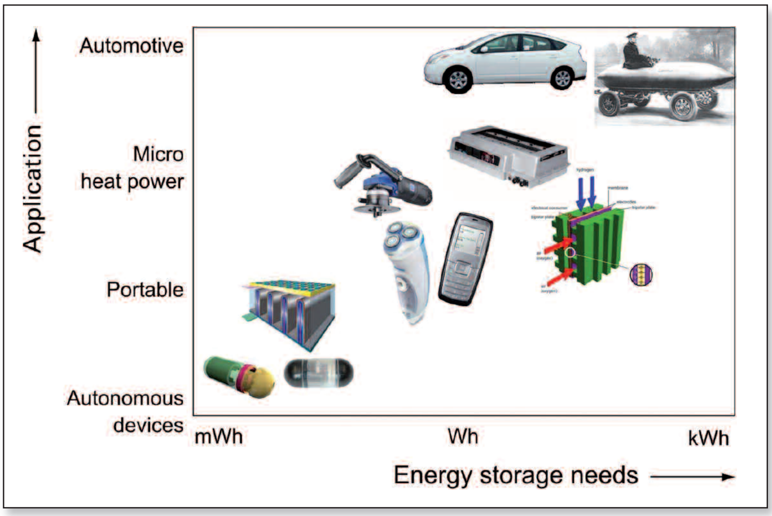
The so-called hybrid cars are evidence of successful large batteries. The future of (plug-in) electrical vehicles, in combination with smart electricity grids, will depend on large-scale rechargeable batteries for storage. Electricity storage is also essential to the feasibility of sustainable energy generated by decentralized, intermittent sources such as solar, wind and tidal power.

At the other end of the "spectrum", small-sized integrated batteries are expected to become more and more important in our daily lives, feeding numerous wireless autonomous devices that will control our future working and living environment. This new electronic revolution has been coined "ambient intelligence" and is considered to be the next challenge in our information-driven age. Already, the use of miniature autonomous devices for medical applications, such as implants controlling our own body, is growing rapidly.

Autonomous devices

Figure 2a shows an example of our future offices and homes equipped with wireless sensors. It features a powerful central computer connected to the internet and communicating with the outside world. The walls of these buildings will be littered by autonomous devices, like specks of dust or *smart dust*, measuring and controlling physical parameters such as temperature, humidity and light intensity. Another example of autonomous devices is medical implants used to stimulate nerves and muscles and to deliver drugs *in vivo* by miniaturized electronic pills see Figure 2b.

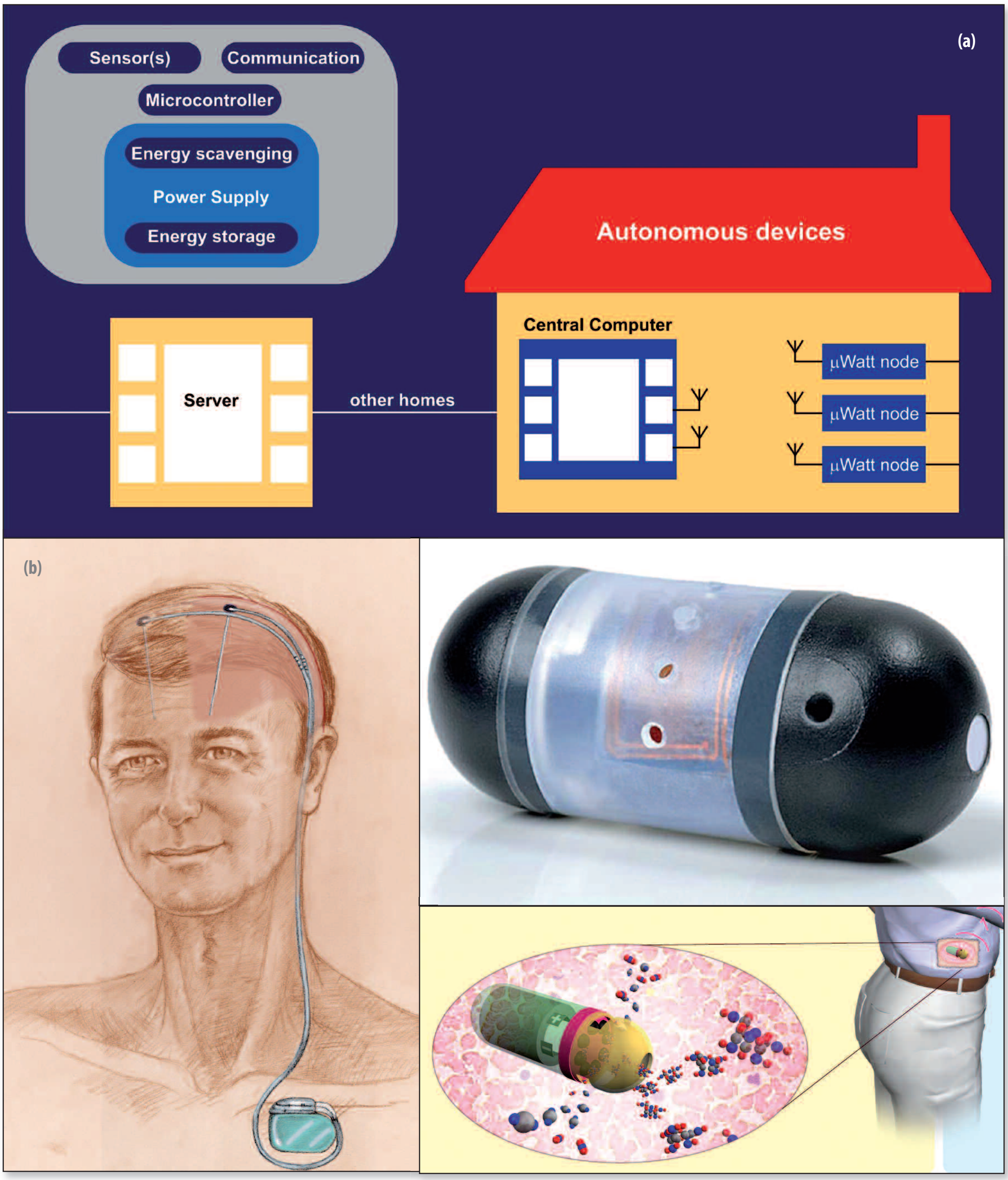
Characteristic for small autonomous devices is the need for wireless operation, implying that on-board electricity is essential. When devices are becoming smaller it becomes more complicated to assemble



these from individual components, whilst the share of inactive overhead material, *e.g.* the package, increases significantly. This leads to on-chip integration of sensor and controller. As the energy consumption will be small, this opens up the further possibility to also integrate the battery. Here, all-solid-state batteries are preferred as this excludes the risk of liquid electrolyte leakage.

Electricity can be stored effectively in either capacitors or batteries. In capacitors, charge carriers are physically accumulating at the electrode/dielectric interface. Since the energy stored in capacitors is proportional to the interface area, one way to increase the amount of charge is to enlarge the active surface area. More efficient storage of electrical energy can be achieved in batteries,

▲ **FIG. 1:** In the near future, rechargeable batteries will power a wide variety of electronic applications. This will range from electrical vehicles, to micro co-generation units, to portable consumer electronics, to small-sized autonomous wireless devices, each characterized by its energy storage needs.



▶ **FIG. 2:** (a) Communication inside our future offices and houses by means of wireless sensor nodes creating ambient intelligence (see text). The inset at the upper left side shows in somewhat more detail the various functions of these wireless sensors. (b) Examples illustrating integrated all-solid-state batteries in future medical applications, including implants for nerve/muscle stimulation and drug delivery by implanted electronic pills.

because electrons not only accumulate at the electrode/electrolyte interface, but also are converted into chemical energy, which subsequently is stored inside the battery electrodes. This results in at least a four orders of magnitude increase of the energy density in batteries in comparison with capacitors [4].

Unfortunately, the energy density of existing planar all-solid-state batteries is rather poor considering the energy demand of many autonomous devices. These planar systems are based on metallic lithium serving as anode with N-doped $Li_3(PO)_4$ (LiPON) serving as solid-state electrolyte [6]. The use of the extremely reactive metallic lithium requires an expensive packaging technology. Moreover, pure lithium is highly volatile and melts at about 181°C, a temperature lower than the soldering temperature usually applied in the electronic industry. Therefore, it would be an advantage to make use of the more stable, so-called intercalation materials, which can store lithium safely at high energy density inside the electrodes. Several new concepts have been proposed all based on 3D-batteries, making use of the combined effect of intercalation materials and surface area enlargement [7]. One of these methods exploits modern IC-technology and makes use of the excellent storage capabilities of thin film silicon anodes, as will be highlighted below.

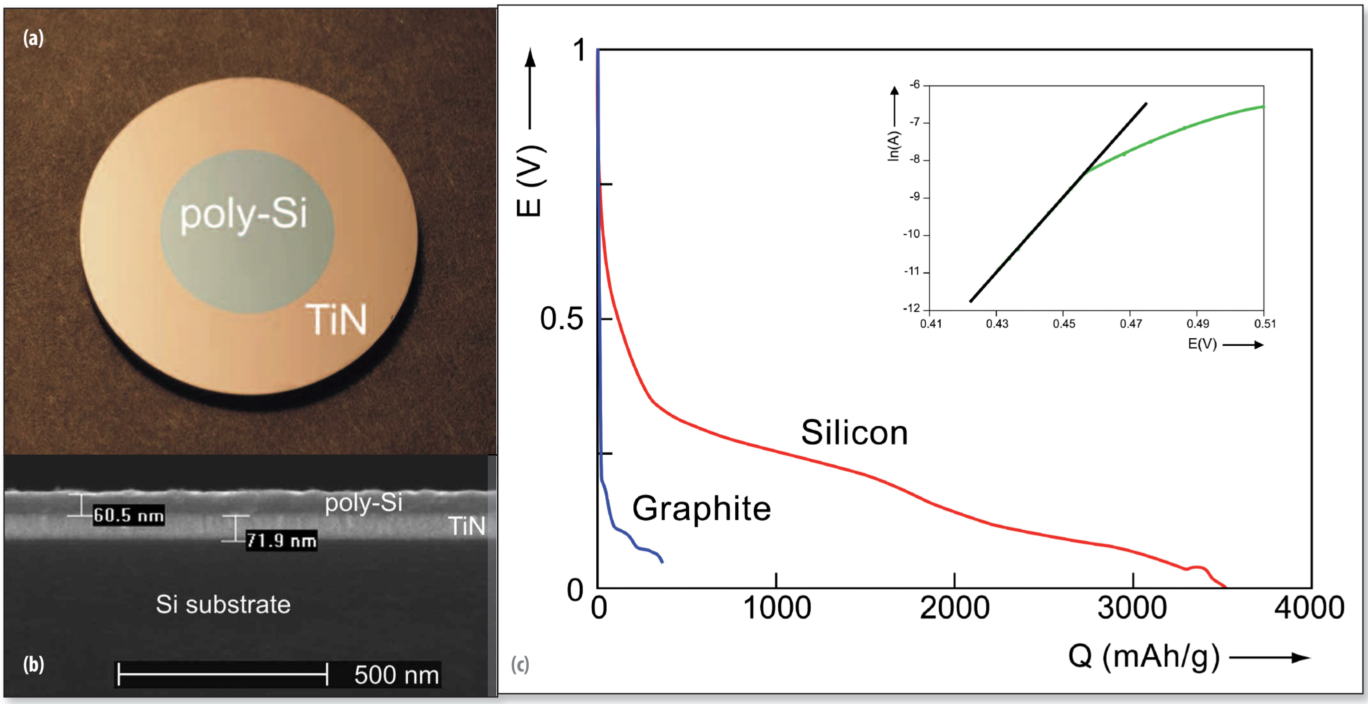
Electrochemical storage of Lithium in Silicon

Silicon is an excellent intercalation material for lithium. According to the phase diagram approximately four lithium atoms can be stored per silicon atom, making this electrode material extremely high energy dense. As a consequence of the high lithium content, the volume expansion is also extraordinary, inducing repeated decrepitation of silicon upon lithium during storage and release [4]. This causes severe contact problems inside the electrode and hence a poor cycle life.

It has, however, been shown that thin films of silicon are mechanically much more stable, because the lattice expansion only takes place normal to the surface [8]. In order to study such thin-film electrodes electrochemically, a silicon wafer has been fully covered with a 70 nm thick TiN barrier layer followed by a well-defined surface area of 60 nm thick poly-silicon, acting as anode, see top-view in Figure 3a. A cross-section of such configuration is shown in Figure 3b. TiN serves both as electronic conducting material and as ionic barrier for lithium ions, preventing lithium from diffusing into the silicon substrate [9] The amount of active silicon in the thin film has accurately been quantified by Rutherford Backscattering Spectrometry (RBS) [5].

Figure 3c shows the lithium storage performance of a silicon thin-film electrode when applying a constant current I. The silicon electrode voltage E has been measured with respect to a metallic lithium reference electrode and the amount of charge $Q = \int I{\cdot}dt$ is plotted on the abscissa. Several intercalation stages can be distinguished in the voltage curve, corresponding to various nano-crystalline phase transitions. Applying different currents and plotting these as a function of the electrode potential, a semi-logarithmic dependence is to be expected, in line with general electrochemical rate laws for charge transfer reactions [5]. Deviation from this linear behaviour beyond ln(A) = -8, *i.e.*, (dis)charging in less than 10 minutes, is due to lithium diffusion limitations inside the silicon electrode. The life cycle performance was found

▼ **FIG. 3:** Top view (a) and cross-section (b) of a silicon thin film (60 nm) electrode deposited by *Low-Pressure Chemical Vapor Deposition* on a 70 nm thick TiN barrier layer, deposited by *Atomic Layer Deposition*. Graphs of the electrode voltage *E* vs. stored charge *Q* (c) show that silicon has a much higher reversible storage capacity than graphite, which nowadays is the standard anode material in almost all conventional Li-ion batteries. The inset shows that the charge transfer reaction is rate-determining up to high currents. At higher currents deviation from this straight line indicates that ionic transport of lithium ions in these thin films start to play a role. Reproduced with permission from Wiley [5].



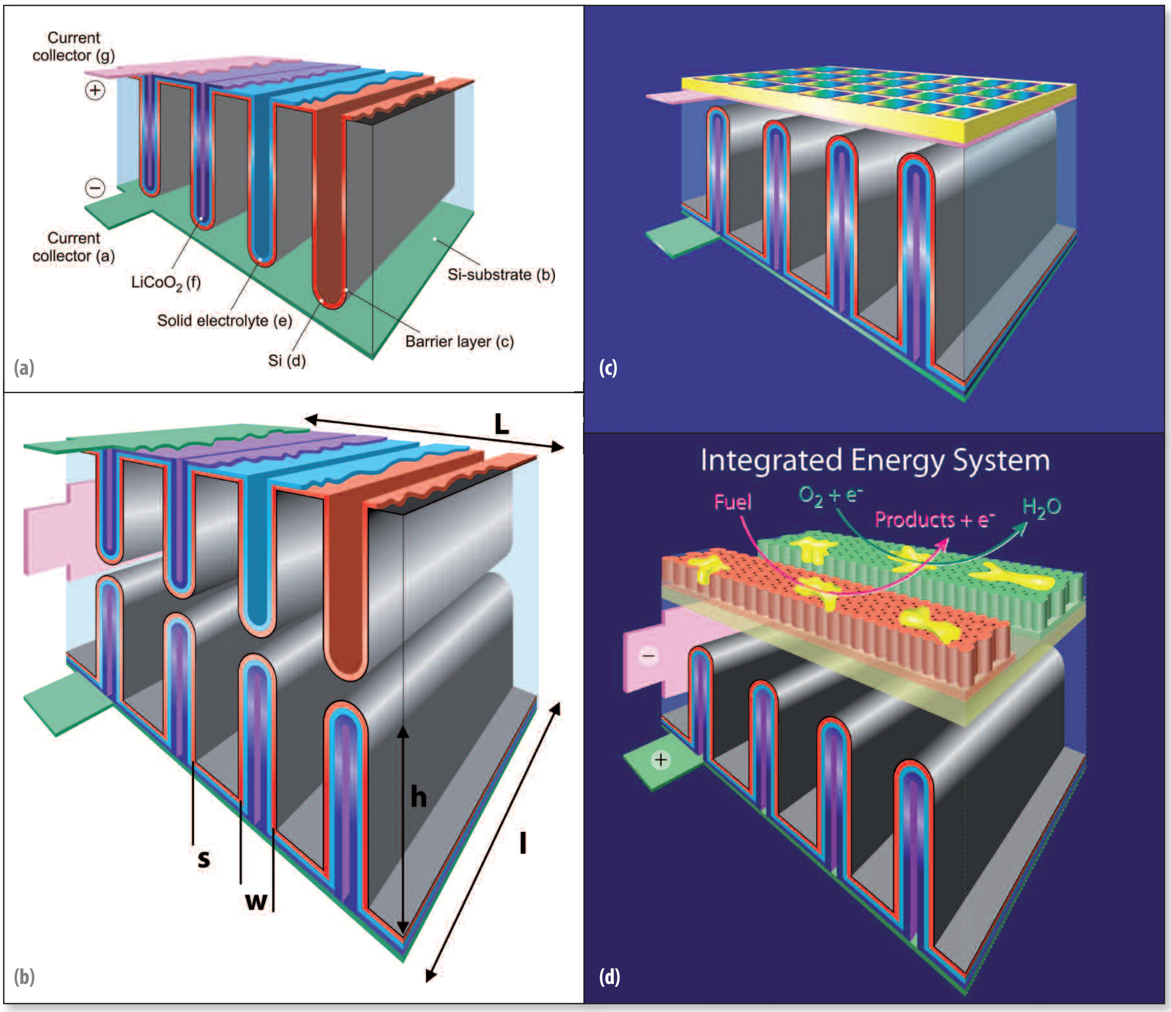


FIG. 4: 3D-integrated all-solid-state battery for powering autonomous devices. (a) The various layers indicated are deposited in high-aspect-ratio trenches etched in, for example, silicon. (b) The geometry of the structure is characterized by footprint dimensions (*L* and *l*), trench height (*h*) and width (*w*) and the spacing between successive trenches (*s*). (c) and (d) Autonomous power supply unit consisting of 3D-integrated all-solid-state lithium-ion batteries combined with electricity generating devices, such as a photovoltaic cell (c) and a bio-inspired fuel cell (d). Reproduced with permission from Wiley [4,10].

to be excellent with the silicon electrode covered by solid-state electrolyte, showing hardly any degradation, thus making these electrodes suitable for long life application [4].

The most striking aspect, however, is the extremely high energy density compared with graphite electrodes used in conventional Li-ion batteries as anode material. Only 372 mAh/g can be stored reversibly in graphite compared with ~3500 mAh/g in silicon. This truly is an impressive improvement in energy density and, together with the long cycle-life, makes it an attractive system to be implemented in 3-D integrated all-solid-state batteries.

3D-integrated all-solid-state battery concept

All-solid-state integrated batteries consist of thin-film barrier layers covering anisotropically etched single-crystal silicon, yielding a large surface area substrate as is illustrated in Figure 4a. Subsequently, various active battery layers are deposited homogeneously inside this structured substrate, starting with a thin film Si-anode, a solid-state electrolyte and a thin film acting as cathode (*e.g.*, $LiCoO_2$). In order to match the lithium capacity of both electrodes, the cathode should be about 20 times thicker than the Si-anode. Deposition of a second current collector completes the 3D-battery integration. Defining the dimensions of the 3D-trench structure (Figure 4b) by width (*w*), height (*h*) and spacing between trenches (*s*) plus the characteristics of the electrode and electrolyte materials, the surface area enlargement (*A*) can be calculated according to

$$A = l + 2h\,\frac{L-s}{L(w+s)} \qquad (1)$$

where *L* and *l* represents the footprint dimensions. Using standard etching technology, an area enlargement of 25 can easily be achieved [5]. Such surface area enlargement combined with the energy densities of the active materials, result in 3D-integrated batteries with energy density of ~1.5 mAh·$\mu m^{-1}cm^{-2}$ footprint area. With an operating voltage of about 3.5 V, a single-sided device is therefore expected to store ~5 mWh·$\mu m^{-1}cm^{-2}$. Obviously, a double-sided process will further increase these numbers. Some experimental results towards 3D-integrated batteries are shown in Figure 5, including *Reactive Ion Etched* trenches (a) and holes (b). Using *Chemical Vapor Deposition* and/or *Atomic Layer Deposition* various active layers have been step-conformal deposited, examples of which are 3D-Si anodes (c) and 3D-$LiCoO_2$ cathodes (d) [10].

Outlook

A new 3D-integrated all-solid-state battery concept has been presented [4,5] This concept is based on the step-conformal deposition of various (in)active layers on a high surface area silicon substrates obtained by micro-etching. Due to the large surface area enhancement, the proposed battery concept will improve the storage capacity of future 3D-integrated all-solid-state Li-ion micro-batteries significantly and offers interesting integration options. In future, fully autonomous power supply units can be designed by combining this battery concept with an electricity-generating device. In case of light being available, a solar cell combination is very effective (Fig. 4c). When light is lacking, as is the case for medical implants, an integrated bio-inspired fuel-cell running on glucose may be employed (Fig. 4d). Recently, a mathematical model has been developed that simulates the power and energy performance of these 3D-integrated all-solid-state devices in their various applications [11]. ■

Acknowledgements

The author would like to acknowledge all co-workers for their valuable contributions during the years in both the experimental and theoretical development of the 3D-integrated battery concept. Frans Schraven and Henny Herps are acknowledged for making the drawings.

About the Author

Peter H.L. Notten was born in The Netherlands in 1952, was educated in analytical chemistry and joined the Philips Research laboratories from 1975 to 2010. While working at these laboratories he received his PhD from the Eindhoven University of Technology (TU/e) in 1989. Since 2000 he has been appointed as part-time professor at the Eindhoven University of Technology. In 2010 he obtained a permanent position at TU/e where he now is heading the group Energy Materials and Devices.

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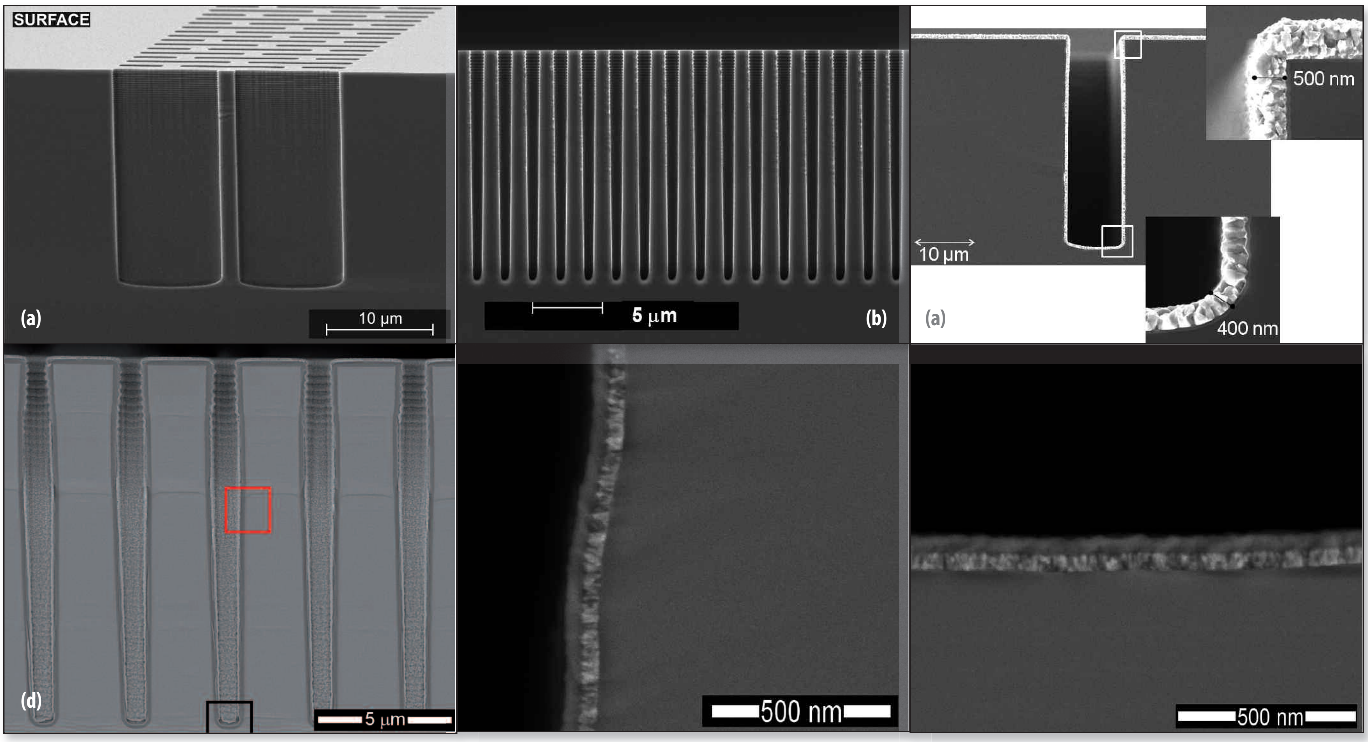

▼ FIG. 5: High-aspect-ratio etching of trenches (a) and pores (b) in mono-crystalline silicon. High-aspect-ratio deposition of a 60 nm silicon anode thin film on top of a 70 nm TiN barrier layer (c) and 500 nm thick $LiCoO_2$ cathode thin film (d) inside trenches [10].