MICROFLUIDICS

Bridges between two worlds

Nanoscale glass can be switched between insulating and conducting states, allowing all-glass microfluidic devices to be made.

Jan Eijkel and Albert van den Berg

Micro- and nanofluidic devices often rely on electricity to perform tasks ranging from DNA sequencing to drug delivery. Electric currents may be used to power a mechanical actuator, or charge an electrical sensor. The use of electricity also brings with it, however, a persistent fabrication dilemma: how can the gap between the world of the electron and the world of the ion be bridged? In the electron world there are metal electrodes connecting circuits together, whereas in the fluidic world aqueous salt solutions course through tiny channels. Traditional approaches can involve precise machining requirements, and unwanted reactions. Writing in *Nature Nanotechnology*, Sanghyun Lee of POSTECH in South Korea and Ran An and Alan Hunt of the University of Michigan solve this challenge using only glass[1].

Interfacing electric current into a fluidic device must involve a transfer of metallic charge carriers (electrons) to charge carriers in solution (ions). The most straightforward way to do this is to integrate metal electrodes directly into the fluidic channels with micromachining. However, this approach has several disadvantages. The biggest is that the electron transfer between the electrode and the solution necessarily involves some local redox reaction, which disturbs the chemical environment inside the channels. Furthermore, it is necessary to machine the components with nanoscale precision to avoid tiny gaps between the dissimilar materials, and this is very difficult and increases cost.

The most common approach to solving the interfacing dilemma is therefore to avoid electrode integration altogether, and place the electrodes in fluid reservoirs that are attached to the fluid channels in the nanofluidic device. Although this approach often works, it introduces a coupling between fluid flow and electric current flow that is sometimes undesirable.

A traditional alternative approach is to place a porous glass composite called a frit between the channel and the electrode. Electric currents can be carried across the frit by ions in the solution. The nanopores in frits have a very low resistance to electric current but a very high resistance to fluid
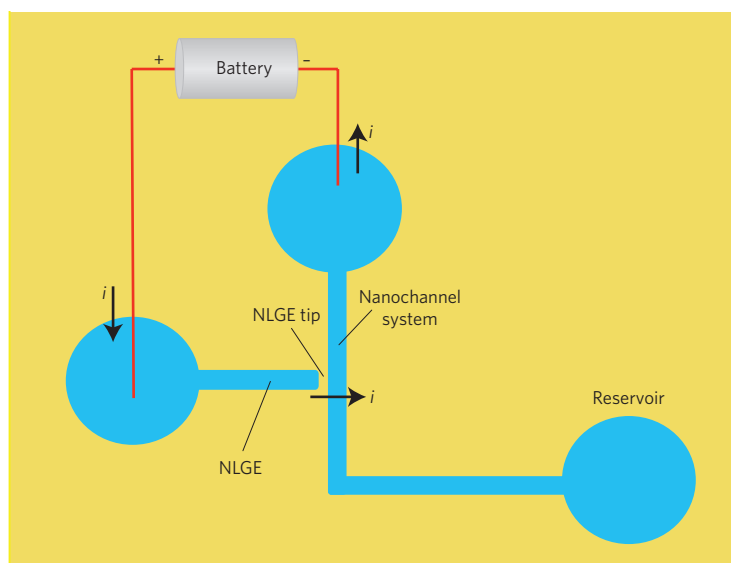

Figure 1 | A nanoscale liquid glass electrode is used to inject current into a nanochannel system. Yellow space represents glass, and blue space represents fluid. A nanochannel and the ultrathin (200 nm) glass wall interfacing to the right nanochannel system comprises the NLGE. The glass wall undergoes reversible dielectric breakdown at high electric fields, allowing it to pass a current (*i*) between the NLGE and the nanochannel system. This current can drive the operation of the system, for example as a pump. The channel system, reservoirs and the NLGE are laser-machined out of a single glass substrate.

flow, so the frit can be regarded as a kind of glassy electrode. Indeed, frits are often used as reference electrodes in electrochemical testing cells.

Another approach was demonstrated by Michael Ramsey and colleagues[2] in 1999 when they micromachined a nanoporous glass membrane in a microfluidic device, which they then used to concentrate samples of DNA before subjecting them to electrophoretic analysis. Nafion membranes, which have subnanometre pores that totally prevent hydrodynamic flow, can also be integrated into nanofluidic devices such as electrokinetic pumps[3].

All of these methods require dissimilar materials to work together or to be attached to each other, increasing both the fabrication and operational complexity. Hunt and colleagues[1] also use porous glass electrodes, but their electrodes are made in and from the same monolithic glass substrate that is used to make the channels themselves. This is made possible by a recently developed

pulsed-laser micromachining method that is eminently suited for the production of nanofluidic channels.

Hunt and colleagues show that thin (200 nm) layers of glass between two nanochannels become conductive above a certain threshold voltage (the 'on' state), so that they can then be used for current injection. They dub the combination of this glass nanolayer with the liquid-filled channel (the 'wire') that runs to it, a nanoscale liquid glass electrode (NLGE). The authors use 3D-laser micromachining to integrate NLGEs into a nanofluidic electrokinetic pump about the size of a red blood cell, the smallest pump of its sort demonstrated so far. Their approach should also simplify non-planar devices, because only a single material is used and also because laser machining is well suited for 3D fabrication.

The authors analyse their electrodes in the electrical domain using a model normally employed for Zener diodes, although they do not directly attribute the currents to electron

transport (see the discussion below). They also perform a thermal analysis, which shows that, despite the high local fields and current densities in the electrodes, the temperature in the 'on' state is only a few degrees above that in the 'off' state, due to excellent heat conduction at the nanoscale. This might explain why the dielectric breakdown that leads to the 'on' state is reversible. The ability to turn the electrode 'on' or 'off' with an applied field is a rather attractive feature because it reduces the chances of inadvertent current leakage.

The paper also leaves us with an intriguing question that deserves further research: what are the charge carriers in the electrodes? The authors argue against ionic conduction because they do not observe any accumulation and depletion of salt at the opposite sides of the 200-nm nanolayers, called concentration polarization. However, it is hard to see how electronic conduction could occur, because this would involve local redox reactions at the solution/glass interface, and such reactions would still cause accumulation of reaction products at the liquid/nanolayer interfaces. Conduction through glass (in, for example, glass pH electrodes) has been studied for many years and has been attributed to proton or sodium ion transport[4,5], amongst others. If these ions are the charge carriers in nanoscale liquid glass electrodes, they would be injectors of specific ions rather than of electrons. Redox reactions would be avoided and a range of interesting new possibilities would be opened up.

We expect that laser micromachining will be predominantly a research and prototyping tool, because of its one-off character and the high cost of the equipment involved. However, the work by Hunt and colleagues[1] shows how well it can serve that purpose and the unprecedented devices that can result. ❑

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INTERFACES

AFM extends its reach

A commercial atomic force microscope can be used to image solid surfaces in liquids and measure interfacial energies with atomic resolution.

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Surfaces and interfaces exhibit a variety of fascinating properties that can be harnessed for applications such as catalysis, electronics and energy conversion[1]. Solid/liquid interfaces are of particular significance and are critical in elementary phenomena as diverse as wettability and crystal growth. The properties of such interfaces can be characterized by their interface energy, which is defined as the sum of the two surface energies, minus the work of adhesion required to separate them. Conventional experimental approaches to determine the interface energy, such as contact-angle measurements, are inherently macroscopic and average over large areas, thereby neglecting local effects due to the structure of the surface or interface at the nanoscale[2]. However, because most of the atoms in a nanostructure reside at its surface, there is a pressing need for experimental techniques that are capable of measuring surface structures and interface energies with high spatial resolution.

Scanning probe microscopy[3] comprises a suite of experimental techniques based on the interaction between a sharp tip and a surface, which can provide morphological images of substrates. In atomic force microscopy[4], the interaction between the tip and the surface is determined by a combination of forces (mainly van der Waals, electrostatic and
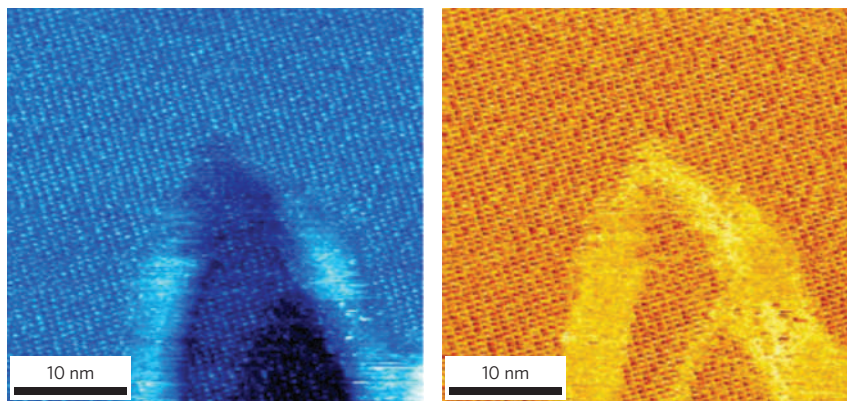

Figure 1 | Mapping solid–liquid adhesion energy with an AFM. Small-amplitude-modulation atomic force microscopy images of calcite ($CaCO_3$) in ultrapure water. A topographic image is shown in blue and a phase image, which maps the phase of the cantilever oscillation during a scan, is shown in yellow. (Figure courtesy of F. Stellacci).

solvation forces), which decay as a power law with respect to distance. The atomic force microscope (AFM) has undergone a number of major advances in recent years: for example, it was recently used to image submolecular features in individual molecules[5] and to measure the force required to move a single atom[6].

Writing in *Nature Nanotechnology*, Kislon Voïtchovsky of the Massachusetts Institute of Technology (MIT) and co-workers now report how a commercial AFM can be used to measure relative interface energies at solid/liquid interfaces[7]. The approach also allows atomically resolved images of various surfaces immersed in liquids, including mica and calcite surfaces in water, to be obtained (Fig. 1); such high resolution has been previously observed only in a handful of cases at the solid/liquid interface.

The experiments of Voïtchovsky and colleagues — who are based at MIT, Oxford,