CHEMISTRY

Putting Electrowetting to Work

Voltage pulses that cause changes in fluid shape or movement can be used to drive optical components and miniaturized assays.

Aaron R. Wheeler

Scientists have long been fascinated by the "self-cleaning" lotus leaf and the "fog-collecting" *Stenocara* beetle. In these cases, nature has engineered materials with heterogeneous texture or chemistry to control the tendency of fluids to wet the surface. There has been great interest in developing artificial mimics with similar properties for applications such as antifouling paints and self-cleaning automobile windshields (*1*). An alternative strategy for surface-mediated fluid control is to tune a surface's wettability by applying pulses of electrical energy. This phenomenon, known as electrowetting (*2*, *3*), has the advantage of being dynamic, a property which has made it useful for applications in areas as diverse as optics and laboratory miniaturization.

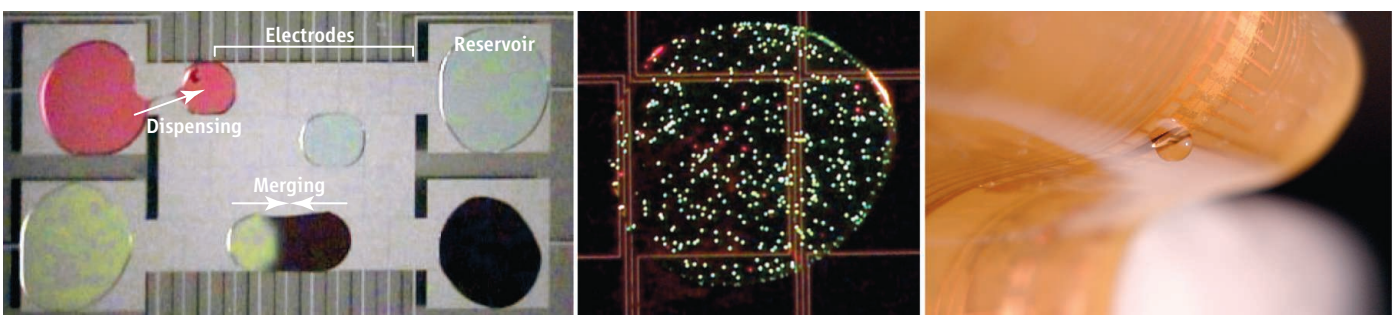
In electrowetting, a fluid is positioned adjacent to an electrode that is coated with a hydrophobic insulator. When a potential, V, is applied across the insulator, it becomes charged, making it attractive for the fluid to wet the surface. For droplets of conductive liquids with relatively large liquid-vapor surface tensions, γ_{lv}, this wetting behavior is approximated by the well-known Young-Lippmann equation: $\cos \theta_w = \cos \theta + \varepsilon_i \varepsilon_o V^2/(2\gamma_{lv}t)$ where θ_w and θ are the wetted and static contact angles, respectively, ε_i and ε_o are the dielectric permittivities of the insulator and vacuum, and t is the thickness of the insulator. In a typical electrowetting device, ~50 to 100 V is applied across a 1-μm thick insulator, causing the contact angle to decrease from $\theta = 115°$ to $\theta_w = 75°$. This behavior is reversible and has attracted interest as a means to exercise dynamic control over fluids on surfaces.

In the past decade, two principal applications have emerged for electrowetting. In the first, electrically driven modulation of fluid shape has been used for optical applications. For example, when a droplet wets a surface, its radius of curvature changes, and the droplet can serve as a lens with a changeable focal length (*4*). Likewise, when a droplet is asymmetrically wetted, its angle of reflection is modulated, allowing it to serve as an active, beam-steering mirror (*5*). Devices powered by these phenomena are now being used in a variety of consumer electronics products [e.g., (*6*, *7*)]. In the second principal application, electrically driven surface energy changes have been used to modulate fluid position in place of (or in addition to) fluid shape (*2*, *3*). It is this application that is the focus here.

To modulate fluid position, droplets are placed on an array of electrodes coated with a hydrophobic insulator. When electrical potentials are applied sequentially to adjacent electrodes, the droplets, which may contain reagents and samples, can be made to move, merge, and dispense from reservoirs (see the figure, left panel). In describing the control of droplet position, the term digital microfluidics is more suitable than electrowetting because there are low-surface tension fluids that can be controlled on such devices but exhibit modest or negligible wetting (that is, $\theta \approx \theta_w$) (*8*). In fact, the motion of fluids as diverse as organic solvents, physiological buffers, ionic liquids, and concentrated surfactants can all be controlled, which allows this technique to serve as a platform for miniaturizing laboratory processes (*9*, *10*).

Digital microfluidics is similar to the more established technology of microfluidic channels in that both can perform lab analyses with much smaller samples than in bench-scale methods. Both methods can manipulate droplets [e.g., (*11*)], which can act as nanoliter vessels for carrying out reactions without cross-talk between samples or reagents. The principal difference is that in digital microfluidics, droplets are addressed individually, whereas in channels, they are controlled in series. Because digital microfluidics is inherently an array-based technique, it is a good match for array-based biochemical applications. In addition, in digital microfluidics, droplets are manipulated on relatively generic platforms (such as an array of M by N electrodes), which are reconfigurable for any desired combination of operations.

An advantage for digital microfluidics is its compatibility with conventional detection instruments. For example, a digital microfluidic array can be interfaced with a fluorescence microplate reader (*12*) by laying out the electrodes to match the pitch and geometry of microtiter plates. Microdroplets with volumes of ~100 nl serve as vehicles for stopped-flow reactions that have much lower fluorescent background and greater sensitivity compared with multiwell plates in many common assays (for example, the detection limit for an alkaline phosphatase assay is 7.0×10^{-20} moles of substrate in a digital microfluidic device versus a detection limit of 5.0×10^{-18} moles in a microtiter plate).



Digital microfluidics for laboratory miniaturization. (**Left**) By applying a sequence of electrical pulses, droplets can be made to move, merge, and dispense on an array of electrodes (these aqueous droplets contain colored dyes and have volumes of 70 nl). (**Middle**) A very low fluorescence background is useful in the analysis of cells in suspension (this 150-nl droplet contains ~250 calcein-labeled Jurkat T cells). (**Right**) Nonplanar substrates greatly enhance the capacity to integrate multiple environments on a single platform. Here, a 1-μl droplet moving upside down is shown.

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Digital microfluidics can also be used in analyses involving biological cells. In a cell-based screen, droplets containing cells, viability reporters, and toxic substrates at different concentrations can be dispensed, mixed, and evaluated with a fluorescence assay (see the figure, middle panel) (*13*). The dose-response curves generated by such devices are more sensitive than equivalent studies on microtiter plates, and cell vitality appears to be unaffected by droplet actuation. Another advantage of digital microfluidics for cell-based assays is the capacity to split and recombine droplets to isolate subpopulations for further analysis (*14*).

Another advantage for the digital microfluidic format is the ease with which electrical components can be integrated into the fluidic circuit. For example, when fabricating an array of droplet-driving electrodes, it is straightforward to also form integrated microheaters for applications that use the polymerase chain reaction. Amplification in such devices can be implemented in half the time and with one-third of the reagent use relative to conventional techniques *(15)*.

As the technology has evolved, the pace of the development of new applications for digital microfluidics has increased. For example, in the past year, Liu *et al*. developed a system for ultra-low–volume DNA ligation (*16*), Luk *et al*. implemented a droplet-based system for proteolytic digestion (*17*), and Fouillet *et al*. reported a technique for carrying out magnetic-bead–based sample processing (*18*). In addition to new applications, there is a regular stream of innovations in digital microfluidic device infrastructure. For example, Chiou *et al*. recently reported the capacity to optically actuate "virtual electrodes," which allows for much greater flexibility in device geometry and design (*19*). Likewise, Abdelgawad *et al*. recently demonstrated digital microfluidic processes on open, nonplanar substrates, which facilitates integration of different physicochemical environments on a common platform (see the figure, right panel) (*20*).

The capacity to use electricity to control the shape and position of droplets on surfaces has led to a dynamic new field of research. Taking a cue from the lotus leaf and the *Stenocara* beetle, we are learning to put surface energies to work, in applications ranging from optics to laboratory miniaturization. Given the trajectory of innovation in this field, it is likely that this work has only just begun.

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GEOLOGY

The Story of O_2

How did biological, geochemical, and geophysical processes produce an atmosphere that allowed complex animal life to evolve?

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Two gases overwhelmingly dominate Earth's atmosphere: N_2 and O_2. The former is primordial, and its presence and abundance are not driven by biological processes. Indeed, N_2 is virtually inert and has an atmospheric lifetime on the order of 1 billion years (*1*). In contrast, O_2 is continuously produced biologically via the oxidation of water driven by energy from the Sun. The gas was almost certainly virtually nonexistent in Earth's early atmosphere, is highly reactive, and has an atmospheric lifetime of ~4 million years (*2*). Yet despite this comparatively short atmospheric lifetime, O_2 came to constitute ~10 to 30% of the atmospheric volume for the past ~500 million years (*3*, *4*).

How did O_2, a gas critical to the evolution of animal life, become the second most abundant gas on Earth? The story is not as simple as it might first appear (*5*, *6*). To understand it, we must know not only how and when O_2 was first generated, but also how it came to persist in high concentrations in the atmosphere.

Elemental oxygen (O) is produced via the so-called "main line" nuclear reaction sequence from successive ^{4}He fusion reactions in hot stars. It was delivered to the early Earth chemically bound to other elements. Through successive cycles of heating and cooling, O reacted with Si and C to form two of the major anions that, together with metal cations, constitute the fundamental minerals in mantle and crust, and with H to form water (*7*). Additional water was delivered to the planetary surface via meteorites and possibly comets; however, the relative proportions of the three sources are not well known (*8*). Regardless of the source, isotopic data suggest that Earth's surface contained liquid water within ~200 million years after the accretion of the planet (*9*). Liquid water is a necessary condition for life as we know it, but it is not a sufficient condition for the biological production of O_2.

Although water can be oxidized to its component elements by ultraviolet light, this reaction can produce only extremely small concentrations of O_2 because of strong negative feedbacks (*10*). The overwhelming source of O_2 on Earth is photobiological oxidation of water; neither the evolution nor the mechanism of this process are completely understood (*11*, *12*). Apparently it arose once in a single clade of bacteria and was then appropriated via a single event, in which one cell engulfed another (endosymbiosis) to form a new symbiotic organism. The latter became the progenitor of all photosynthetic eukaryotes, including algae and higher plants (*12*).

The core of the oxidation machinery is photosystem II, a large protein complex containing four manganese atoms that are photocatalytically oxidized to create electron holes upstream. O_2 is produced as a waste product via the reaction

$$2H_2O \rightarrow 4e + 4H^+ + O_2$$

The protons and electrons generated are used to reduce CO_2 to form organic matter via

$$CO_2 + 4e + 4H^+ \rightarrow (CH_2O) + H_2O$$

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