We wish to report microelectrochemical devices that mimic some functions of solid-state circuit components such as diodes and transistors. The operation of this family of devices is enabled by a network of microfluidic electrochemical cells that communicate via conductive solutions and, in some cases, bipolar electrodes. Networking and cross communication between individual channels represent important challenges that must be addressed in conjunction with the development of integrated, multifunctional microfluidic systems. We view the approach reported here as a first step toward the development of large-scale microfluidic integrated systems having parallel processing capabilities. We envision applications to biological and chemical sensing, process control, and analysis.

There have been previous examples of electrochemical systems that mimic the function of microelectronic circuit elements. In the 1950s, electrochemical cells called solitons were introduced that used electrodes and small orifices or channels to perform such functions as detection, amplification, integration, and rectification. In more modern times, Wrighton and co-workers showed that some characteristics of diodes and field-effect transistors (FETs) could be mimicked by microelectrode arrays coated with conducting polymer films. Amatore et al. used microelectrode arrays to perform Boolean logic operations. Although there are no examples in the literature of electronic device functions having been demonstrated using microfluidic electrochemical systems, fluidics alone were used to construct sophisticated control systems as early as the 1960s. Recently such systems have been adapted to microfluidic formats.

The cell design used here is shown in Figure 1. The cell contains poly(dimethylsiloxane) (PDMS) channels and indium tin oxide (ITO) electrodes patterned onto glass using standard photolithographic methods. The device is assembled by aligning the PDMS channel network over the electrodes, and then sealing the two parts together. A micrograph of the completed assembly is shown in Figure 1B.

A schematic illustration of one device configuration, a diode, is shown in Figure 1C. In such a design, aqueous solutions of Ru(NH$_3$)$_6^{3+}$, Ru(bpy)$_2^{2+}$ (bpy = 2,2'-bipyridine), and electrolyte solution only are passed through channels 1, 2, and 3, respectively, at the same flow rate. These three fluids move under laminar flow conditions and exit the device through the large channel at the top of the device. When a forward bias of 1.5 V is applied between electrodes 1 and 2 ($E_{1,2}$), where electrodes 1 and 2 are configured as the cathode and anode, respectively, and electrode 3 is at open circuit, Ru(NH$_3$)$_6^{3+}$ is reduced and Ru(bpy)$_2^{2+}$ is oxidized (eqs 1 and 2) resulting in a current ($i_{1,2}$) of $\sim$100 nA (Figure 2A). When the device is reverse-biased at the same voltage, $i_{1,2}$ is less than 2 nA. This behavior is a thermodynamic consequence of the relative ease with which the two reagents can be oxidized and reduced. That is, Ru(NH$_3$)$_6^{3+}$ is easy to reduce but difficult to oxidize, while the opposite is true for Ru(bpy)$_2^{2+}$. Diode-like half-wave rectification is shown in Figure 2B. Here, $E_{1,2}$ was pulsed between +1.5 and -1.5 V, but a significant current only flows at forward bias. When one or both redox molecules are absent, diode-like behavior is not observed until oxidation or reduction of the electrolyte solution itself occurs (Figure 2A).

$$\text{Ru(NH}_3\text{)}_6^{3+} + e^- = \text{Ru(NH}_3\text{)}_6^{2+} \quad (-0.15 \text{ V})$$

(1)

$$\text{Ru(bpy)}_2^{2+} - e^- = \text{Ru(bpy)}_2^{3+} \quad (0.92 \text{ V})$$

(2)

$$\text{Fe(CN)}_6^{3-} + e^- = \text{Fe(CN)}_6^{4-} \quad (0.12 \text{ V})$$

(3)

It is possible to modulate the forward-bias current of the device described in the previous paragraph by applying a gate bias between electrodes 2 and 3 ($E_{2,3}$). In this case (Figure 1C), a 1.0 mM solution of Fe(CN)$_6^{3-}$, which is more easily reduced than Ru(NH$_3$)$_6^{3+}$ (eq 3), competes for electrons with Ru(NH$_3$)$_6^{3+}$ and thereby reduces the magnitude of $i_{1,2}$. Figure 2C shows a family of linear sweep voltammograms (LSVs) obtained by scanning $E_{1,2}$ from 0.5 to 2.0 V, while holding $E_{2,3}$ constant at values ranging from 0.8 to 1.5 V. For example, when $E_{2,3}$ is set to 1.1 V, $i_{1,2}$ < 2 nA when $E_{1,2}$ < 1.25 V. In contrast, when $E_{2,3}$ = 0.8 V, $i_{1,2}$ > 40 nA at $E_{1,2}$ = 1.25 V. Note that only if electrolyte solution is used in channel 3, no gating effect is observed over the range of biases ($E_{2,3}$) shown in Figure 2C (LSV indicated as 1.5(C) in Figure 2C).

This same general approach can be used to construct optoelectrochemical logic gates. For example, Figure 3A shows the configuration used to fabricate an OR gate. In this case, a Ru(NH$_3$)$_6^{3+}$ solution flows in both channels 1 and 2, and Ru(bpy)$_2^{2+}$ plus tripropylamine (TPA) flows in channel 3. Under conditions that lead to the oxidation of Ru(bpy)$_2^{2+}$ and TPA, electrogemmed chemiluminescence (ECL) is emitted from electrode 3, which is the output of this logic gate. As shown in Figure 3B, either one (or both) of these two Ru(NH$_3$)$_6^{3+}$ streams can couple with the ECL process, thereby resulting in light emission. Specifically, when $E_{1,2}$ and $E_{2,3}$ are at open circuit, no current flows, and therefore no light is observed (Figure 3B). When $E_{1,3}$ and $E_{2,3}$, or $E_{1,3}$ and $E_{2,3}$ = 1.5 V, the output is determined by the relative magnitude of $i_{1,2}$ and $i_{2,3}$.
Figure 3) is passed through each of the nine numbered channels of a NAND logic gate. One of four different redox solutions (see caption, Figure 3A) was present in channel 3. A control experiment was performed by holding \( E_{2,3} \) (Figure 1C) at 1.5 V with only electrolyte solution in channel 3. As shown in the truth table (inset of Figure 3B), when the discriminator level is set at the ECL intensity shown by the dashed red line in Figure 3D, the ECL signal is further suppressed, and the device is off. Thus, this device generates the truth table corresponding to a NAND gate (inset of Figure 3D), when the discriminator level is set at the ECL intensity shown by the dashed red line in Figure 3D.

In summary, we have described microelectrochemical systems that mimic some functions of diodes, FETs, and logic gates. Like solid-state devices, these electrochemical systems are modular, and thus, module integration leads to more complex functions. These electrochemical systems rely on mass transport of fluids, however, and therefore, their time response is much slower than field-effect devices. Accordingly, they are more likely to find applications in sensing and process control than as replacements for solid-state electronic devices.

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References

(11) The magnitudes of all currents are given as absolute values.
(12) These onset potentials (vs a Ag quasi reference electrode) correspond to a faradaic current 3 times above background and were determined by cyclic voltammetry using a three-electrode microfluidic electrochemical cell under flowing conditions.

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