

## Microelectrochemical Logic Circuits

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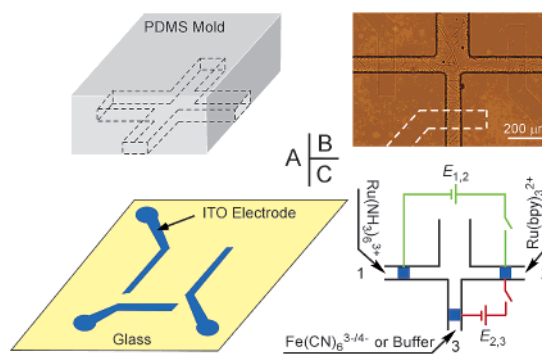
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We wish to report microelectrochemical devices that mimic some functions of solid-state circuit components such as diodes and transistors. The operation of this family of devices is enabled by a network of microfluidic electrochemical cells that communicate 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 integrated electrochemical systems having parallel processing capabilities.<sup>1</sup> 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 solions were introduced that used electrodes and small orifices or channels to perform such functions as detection, amplification, integration, and rectification.<sup>2</sup> In more modern times, Wrighton and co-workers showed that some characteristics of diodes<sup>3</sup> and field-effect transistors (FETs)<sup>4</sup> could be mimicked by microelectrode arrays coated with conducting polymer films. Amatore et al. used microelectrode arrays to perform Boolean logic operations.<sup>5</sup> 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.<sup>6</sup> Recently such systems have been adapted to microfluidic formats.<sup>7</sup>

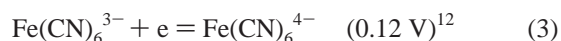
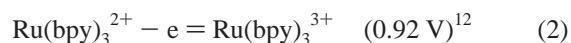
The cell design used here is shown in Figure 1. The electrochemical microfluidic system comprises poly(dimethylsiloxane) (PDMS) channels<sup>8</sup> and indium tin oxide (ITO) electrodes patterned onto glass using standard photolithographic methods<sup>9</sup> (Figure 1A). The device is assembled by aligning the PDMS channel network over the electrodes, and then sealing the two parts together.<sup>9</sup> 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 this case, aqueous solutions of  $\text{Ru}(\text{NH}_3)_6^{3+}$ ,  $\text{Ru}(\text{bpy})_3^{2+}$  (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<sup>10</sup> 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,  $\text{Ru}(\text{NH}_3)_6^{3+}$  is reduced and  $\text{Ru}(\text{bpy})_3^{2+}$  is oxidized (eqs 1 and 2) resulting in a current ( $i_{1,2}$ )<sup>11</sup> 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,  $\text{Ru}(\text{NH}_3)_6^{3+}$  is easy to reduce but difficult to oxidize, while the opposite is true for  $\text{Ru}(\text{bpy})_3^{2+}$ . 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



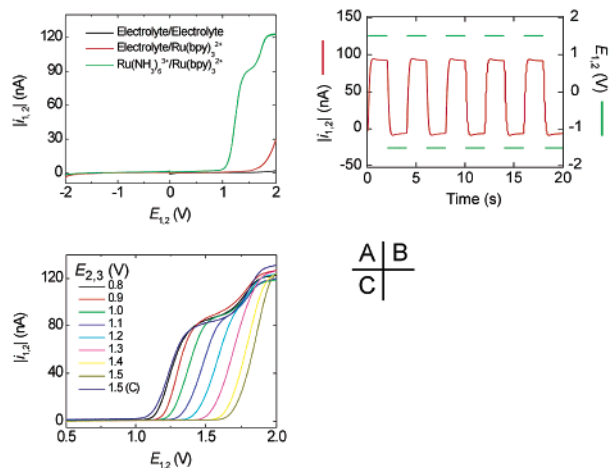
**Figure 1.** (A) Schematic illustration showing the assembly of the microelectrochemical device. The channels are  $100 \mu\text{m}$  wide and  $17 \mu\text{m}$  high, and the area of the ITO microelectrodes is  $10^4 \mu\text{m}^2$ . (B) Micrograph of the device illustrated in (A). The device contains three input channels and a common outlet. A transparent ITO microelectrode is highlighted by the white dashed line. (C) A microelectrochemical device configuration that mimics diode and FET behavior.

observed until oxidation or reduction of the electrolyte solution itself occurs (Figure 2A).

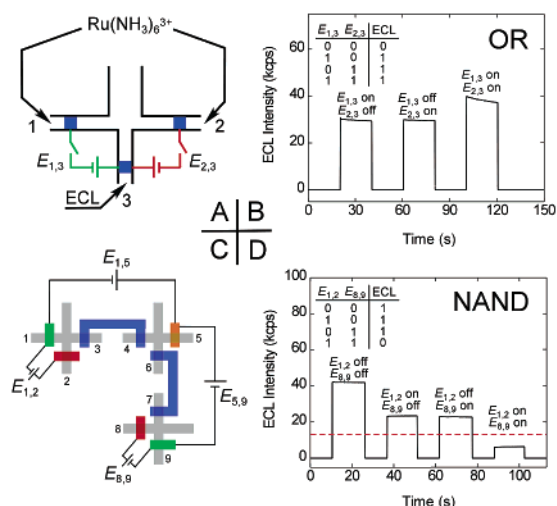


It is possible to modulate the forward-bias current of the device described in the previous paragraph by applying a gate bias between electrodes 2 and 3 ( $E_{2,3}$ ). In this case (Figure 1C), a 1.0 mM solution of  $\text{Fe}(\text{CN})_6^{3-}$ , which is more easily reduced than  $\text{Ru}(\text{NH}_3)_6^{3+}$  (eq 3), competes for electrons with  $\text{Ru}(\text{NH}_3)_6^{3+}$  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 when only 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  $\text{Ru}(\text{NH}_3)_6^{3+}$  solution flows in both channels 1 and 2, and  $\text{Ru}(\text{bpy})_3^{2+}$  plus tripropylamine (TPA) flows in channel 3. Under conditions that lead to the oxidation of  $\text{Ru}(\text{bpy})_3^{2+}$  and TPA, electrogenerated chemiluminescence (ECL) is emitted from electrode 3,<sup>13-15</sup> which is the output of this logic gate. As shown in Figure 3B, either one (or both) of these two  $\text{Ru}(\text{NH}_3)_6^{3+}$  streams can couple with the ECL process, thereby resulting in light emission. Specifically, when  $E_{1,3}$  and  $E_{2,3}$  are at open circuit, no current flows, and therefore no light is observed (Figure 3B). When  $E_{1,3}$ ,  $E_{2,3}$ , or  $E_{1,3}$  and  $E_{2,3} =$



**Figure 2.** Characterization of the microelectrochemical system shown in Figure 1. (A) LSVs of a two-electrode diode-like device. Channels 1, 2, and 3 (Figure 1) were filled with 1.0 mM Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup>, 1.0 mM Ru(bpy)<sub>3</sub><sup>2+</sup>, and electrolyte solution, respectively. Electrolyte solution: 0.1 M KCl + 0.1 M phosphate buffer, pH 7.5. Flow rate: 1.0  $\mu$ L/min. (B) Demonstration of half-wave rectification. Conditions are the same as in (A). (C) Demonstration of FET-like behavior. Conditions are the same as in (A), except 1.0 mM Fe(CN)<sub>6</sub><sup>3-</sup> is 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 (LSV 1.5(C)).



**Figure 3.** OR and AND optoelectrochemical logic gates. (A) Schematic diagram of the circuit for an OR gate.  $E_{1,3} = E_{2,3} = 1.9$  V. (B) ECL response obtained from the circuit in (A). Inset: truth table for the OR logic gate. (C) Schematic of the circuit assembly for a NAND gate. The following solutions were flowed through the channels: channel 5, 1.0 mM Ru(bpy)<sub>3</sub><sup>2+</sup>/50 mM tripropylamine; channels 1, 4, 6, and 9, 1.0 mM Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup>; channels 2 and 8, 1.0 mM Fe(CN)<sub>6</sub><sup>4-</sup>; channels 3 and 7, 1.0 mM Ru(bpy)<sub>3</sub><sup>2+</sup>. The electrolyte solution was 0.1 M KCl + 0.1 M phosphate buffer, pH 7.5.  $E_{1,5} = E_{5,9} = 3.0$  V. The device inputs,  $E_{1,2}$  and  $E_{8,9}$ , were set to 1.5 V or were at open circuit. (D) ECL response obtained from the circuit shown in (C). Inset: truth table for NAND logic gate. The red dashed line indicates the discriminator level used to define “1” and “0” states.

1.9 V, then current flows in one or both external circuits, and light emission results. As shown in the truth table (inset of Figure 3B) this behavior constitutes an OR logic gate.

The seven-electrode device shown in Figure 3C functions as a NAND logic gate. One of four different redox solutions (see caption, Figure 3) is passed through each of the nine numbered channels

(shown in gray) of this device. During operation, a 3 V bias is applied between the ECL reporting electrode (shown in orange) and the two coupling electrodes (shown in green), where Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> reduction occurs. Direct coupling between the green and orange electrodes is assisted by two bipolar electrodes (shown in blue), over which sacrificial solutions of either Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> or Ru(bpy)<sub>3</sub><sup>2+</sup> (no TPA) were flowed. Finally, Fe(CN)<sub>6</sub><sup>4-</sup> solutions were flowed over the two electrodes shown in red, which could be directly linked with Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> reduction at the green electrodes when a 1.5 V bias was applied between the red and green electrodes. As a result, when both  $E_{1,2}$  and  $E_{8,9}$  are at open circuit, the ECL signal is evident, and the device is on (Figure 3D). Application of a 1.5 V bias to either  $E_{1,2}$  or  $E_{8,9}$  will turn off electrochemical coupling between the light-emitting electrode (orange) and one of the two green electrodes (but not both). Therefore, the device is still on. When both inputs are connected ( $E_{1,2}$  and  $E_{8,9} = 1.5$  V), 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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