2-5-5. Electrochemical Imaging (Electrochromism and Electrochemiluminescence)

Overview

Electrochemical reactions can trigger optical modulation phenomena collectively termed electrochemical imaging. Among these, electrochromism (EC) and electrochemiluminescence (ECL) are the most prominent (Fig. 1). EC involves reversible color modulation through redox processes, producing absorption changes with minimal viewing-angle dependence and memory effects. It has been applied in antiglare mirrors and smart windows. ECL, in contrast, arises from excited states generated by the recombination of oxidized and reduced species at electrodes. The ability to emit light without external excitation has established ECL as a powerful tool for sensitive analysis and clinical diagnostics.

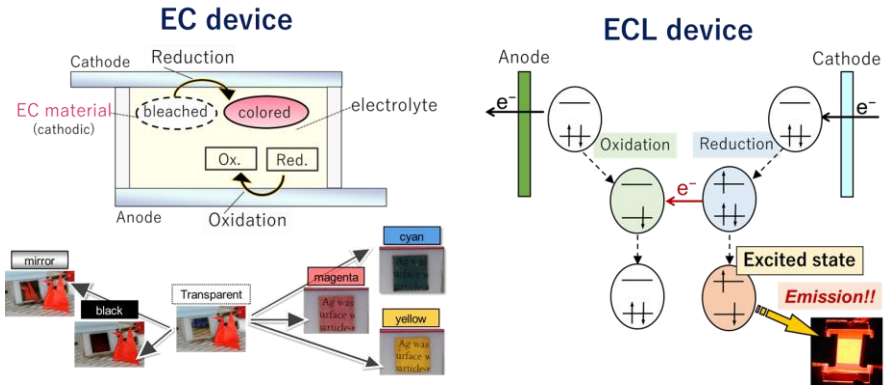

Figure 1. Electrochemical imaging.

Current Status and Frontiers

1. Electrochromism

The research on EC can be traced back to 1969, when K. Deb first reported the reversible coloration and bleaching of tungsten oxide (WO_3). Initially, metal oxides were the main subject of investigation, but subsequent studies expanded to organic molecules such as viologens, conducting polymers, and, more recently, organic–inorganic hybrid materials. In the early 1970s, EC attracted strong interest as a candidate for display applications, and large-scale projects were pursued across the United States, Europe, and Japan. However, issues related to switching speed and durability, along with competition from liquid-crystal technologies, caused a temporary decline in research momentum.

Later, the unique ability of EC to modulate optical transmittance from the transparent to colored states regained attention, particularly in the development of energy-saving smart windows for buildings, antiglare mirrors in automobiles, and aircraft windows. A milestone in EC materials research was achieved by J. R. Reynolds and co-workers, who demonstrated electrochemical doping and de-doping of conjugated polymers for color tuning across the visible to near-infrared region. This work established the foundation for organic EC device research. More recently, novel EC devices utilizing the reversible electrodeposition of metal nanoparticles have been reported. By controlling the size and morphology of the deposited nanoparticles, these systems enable versatile coloration effects beyond black or mirror-like reflection, including a variety of chromatic hues. Furthermore, the intrinsically low power consumption of EC devices has inspired new concepts such as integrated systems combining EC layers with solar cells or

thermoelectric elements. Another emerging direction is the development of electrochromic energy-storage devices, in which the coloration/bleaching process can be regarded as the charge/discharge of a secondary battery, thereby allowing simultaneous optical modulation and energy storage.

2. Electrochemiluminescence

ECL research began in the late 1960s, when A. J. Bard and co-workers reported the ECL emission of the ruthenium complex $Ru(bpy)_3^{2+}$. The most significant advantage of ECL lies in the simplicity of its device configuration: light emission can be achieved using only an electrode and an electrolyte solution, without requiring external light sources. This eliminates background interference that often affects fluorescence and phosphorescence methods. Unlike organic light-emitting diodes (OLEDs), ECL does not require multilayer thin-film structures, making it adaptable to a wide range of device formats including solutions, gels, thick films, and bulk materials.

Due to these advantages, ECL was introduced early into clinical diagnostics and immunoassays. During the 1980s and 1990s, ECL became widely established as a highly sensitive analytical tool through integration with chemiluminescence detection equipment. Today, ECL is regarded as a standard method in blood tests, biomarker detection, and DNA analysis, playing a critical role in modern clinical and bioanalytical science.

In recent years, several new research directions have emerged. In bioanalytical applications, the combination of micro/nanoelectrode arrays with photoluminescence techniques has enabled high-spatial-resolution ECL imaging at the single-cell and subcellular levels, allowing localized chemical reactions to be visualized in situ. In materials development, in addition to traditional Ru complexes and luminol, advanced emitters such as quantum dots, carbon dots, metal nanoclusters, two-dimensional nanosheets, and metal–organic frameworks (MOFs) have been actively explored. These materials provide enhanced ECL efficiencies, tunable emission wavelengths, and improved stability. Near-infrared ECL emission, long-lived luminophores, and highly stable systems have been realized. Furthermore, innovative photofunctional concepts have been introduced, such as electrochemically driven up-conversion luminescence and thermally activated delayed fluorescence (TADF) luminophores, the latter enabling the development of ECL devices with operational lifetimes exceeding 1000 hours.

References

1. P. M. Beaujuge, J. R. Reynolds, *Chem. Rev.*, **110**, 268–320 (2010).
2. A. Tsuboi, K. Nakamura, N. Kobayashi, *Adv. Mater.*, **25**, 3197–3201 (2013).
3. P. Yang, P. Sun, W. Mai, *Materials Today*, **19**, 394–402 (2016).
4. G. Valenti, F. Paolucci, N. Sojic, et al., *J. Am. Chem. Soc.*, **139**, 16830–16837 (2017).
5. L. M. Cavinato, K. Albrecht, R. D. Costa, et al. *Adv. Funct. Mater.*, **33**, 2302483 (2023).

Future Perspectives and Directions

Electrochemical imaging devices have thus far advanced primarily as technologies for optical modulation and sensing. However, challenges remain in improving response speed, efficiency, and durability. Looking ahead, the unique freedom in material selection and device architecture inherent to electrochemical systems can be exploited in combination with diverse photochemical functionalities, enabling the realization of devices that go far beyond conventional optical modulation.

(Author: Kazuki Nakamura)