Scientists unravel the mysteries of irreversibility in electrochromic thin films

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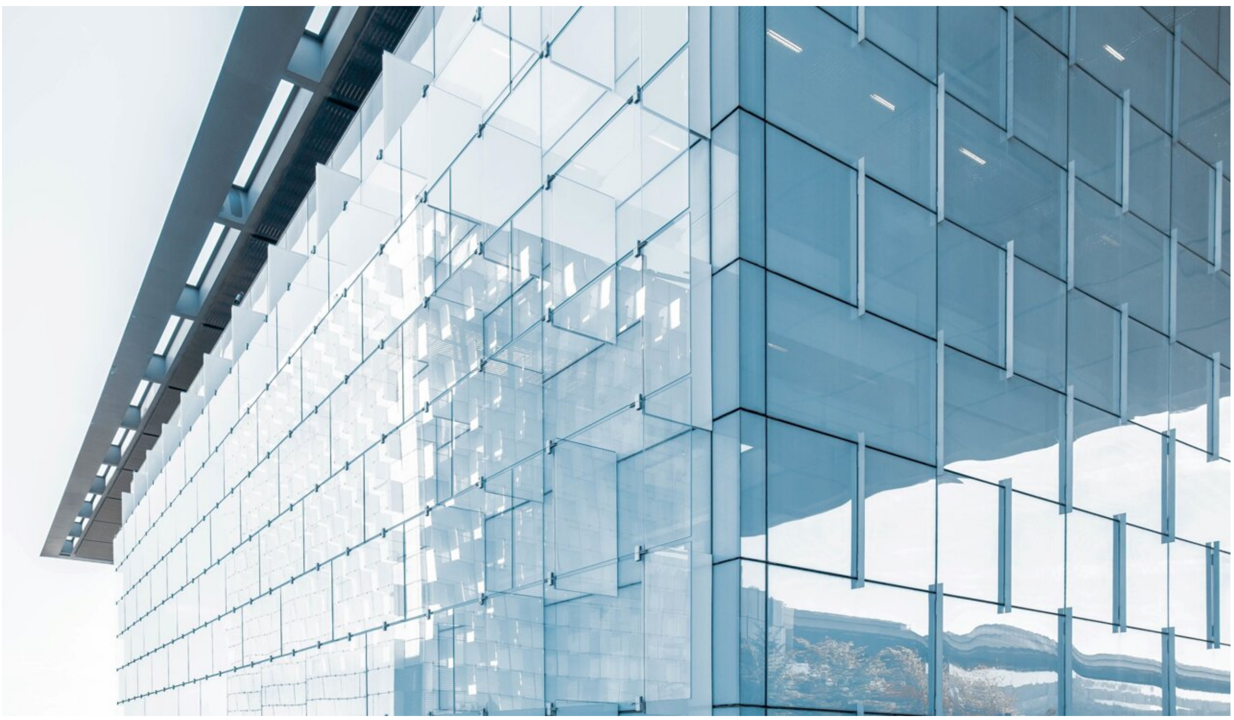

Smart windows, one of the most promising applications of tungsten oxide (WO3) thin films, are transmittance-controllable windows used in automobiles, aircraft, and building applications. Credit: Joel Filipe from Stocksnap

Electrochromic (EC) materials, among the key "green" technological components for sustainability and energy savings, have piqued the interest of academia and industry alike. Tungsten oxide (WO_3) is an extensively researched EC material that is widely used in today's smart windows. One popular EC approach is the reversible insertion of small ions into electrode materials. Thin films of WO_3 can therefore change their color from clear to deep blue by adjusting lithium ion (Li^+) insertion under a low voltage bias. As low voltage operations are beneficial for a multitude of applications, Li^+ intercalated WO_3 (Li_xWO_3) is a viable option for EC device applications.

However, Li^+ insertions are not always reversible. After several cycles, these ions aggregate in the film and erode the electrochromic effect. This, in turn, affects optical modulation and long-term durability, both of which are essential for practical deployment of EC devices. The insertions result in reversible Li^+, irreversible Li_2WO_4 formation, and irreversible Li^+ trapping. The "irreversible formation of Li_2WO_4" degrades electrochromism, and the Li^+ 'trapped' at deep sites renders the ions immobile, resulting in irreversibility. In essence, evaluating the implications of both types of irreversibility is critical.

In a recent study published in *Applied Surface Science*, scientists from Tokyo University of Science and the National Institute for Materials Science (NIMS), Japan, collaborated to quantitatively assess the irreversibility of Li_xWO_3 thin films. Discussing the key concerns that the study addresses, Associate Professor Tohru Higuchi from Tokyo University of Science, who led the study, observes "There are two critical questions that arise: First, is irreversible Li_2WO_4 formation different from irreversible Li^+ trapping? Second, can these irreversible components coexist?" He adds, "Conventional measures are unable to differentiate between the two irreversible components. As a result, we conducted a quantitative examination to offer solid answers to these questions."

The scientists devised a quantitative evaluation method that combines in situ hard X-ray photoelectron spectroscopy (HAXPES) and electrochemical measurements. HAXPES is used to investigate buried interfaces, whereas electrochemical tests are used to examine corrosion properties. The intercalation of Li^+ results in a redox reaction that changes the oxidation state of tungsten (W) ions from W^{6+} to W^{5+}. Based on this change, HAXPES can evaluate "reversible Li^+" and "irreversible Li^+ trapping." However, evaluating "irreversible Li_2WO_4 formation" using HAXPES is challenging. Dr. Takashi Tsuchiya, a principal researcher at NIMS and co-author of the study, explains why: "W ions in Li_2WO_4 have a stable oxidation state because they exist in the W^{6+} form. As a result, HAXPES is unable to evaluate the irreversibility caused by Li_2WO_4 formation. Electrochemical measurements, on the contrary, can distinguish 'reversible Li+' from the two irreversible components. Therefore, integrating both methods enables the distinction and quantitative evaluation of all three components."

To conduct the electrochemical measurements, the scientists built a Li_xWO_3-based redox transistor on the flat surface of a lithium-ion conducting glass ceramic (LICGC). They also built an electrochemical cell with a WO_3 thin film as the semiconductor and a LICGC substrate as the electrolyte to conduct HAXPES measurements. Furthermore, they employed in situ Raman spectroscopy to assess the influence of Li^+ insertion on the Li_xWO_3 structure. They were able to successfully determine the increase in crystallinity caused by Li^+ insertion. The proportions of reversible Li^+, irreversible Li_2WO_4 formation, and irreversible Li^+ trapping were calculated to be 41.4%, 50.9%, and 7.7%, respectively.

The scientists believe that their study will help develop and design improved EC materials and devices. "For several years, the main impetus for EC research and development has been potential applications in energy-efficient buildings and aircraft. However, there are several other applications as well, such as the energy-saving and vision-friendly electronic paper displays," says Dr. Kazuya Terabe, principal investigator of the International Center for Materials

Nanoarchitectonics at NIMS and a co-author of the study, "Moreover, our findings broaden the application possibilities by providing the basis for the future development of high-performance WO_3-based EC devices."

More information: Makoto Takayanagi et al, In situ hard X-ray photoelectron spectroscopy on the origin of irreversibility in electrochromic LixWO3 thin films, *Applied Surface Science* (2021). DOI: 10.1016/j.apsusc.2021.150898

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