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Sustainable rejuvenation of electrochromic WO$_3$ films

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ABSTRACT

Devices relying on ion transport normally suffer from a decline of their long-term performance due to irreversible ion accumulation in the host material, and this effect may severely curtail the operational lifetime of the device. In this work, we demonstrate that degraded electrochromic WO$_3$ films can sustainably regain their initial performance through galvanostatic de-trapping of Li$^+$ ions. The rejuvenated films displayed degradation features similar to those of the as-prepared films, thus indicating that the de-trapping process is effectively reversible so that long-term performance degradation can be successfully avoided. De-trapping did not occur in the absence of an electric current.

Energy conservation is widely recognized as an essential part of a sustainable global energy system.[1] This realization brings attention to the buildings sector, which is responsible for a large and growing part of the global use of energy.[2,3] Energy-efficient fenestration is of considerable interest in this context,[4] and electrochromic (EC) "smart windows" are of particular importance.[5-7] These windows are able to vary their throughput of visible light and solar radiation by the application of a low electrical voltage and can provide energy efficiency along with indoor comfort in buildings.[8-10] Amorphous WO_3 is the most widely studied EC material, and its optical absorption can be varied through Li^+ ion intercalation[11] and accompanying insertion of charge balancing electrons. This mechanism can be expressed, schematically, as[11]

$$WO_3|_{transparent} + x(Li^+ + e^-) \leftrightarrow Li_xWO_3|_{blue} \quad , \qquad (1)$$
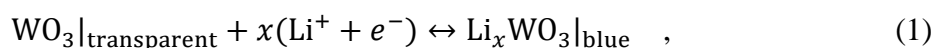
where e^- denotes electrons. Thin films of amorphous WO_3 change from optically transparent to dark blue when Li^+ ions are inserted, and the films return to their transparent state if these ions are extracted.

High optical modulation and long-term durability are needed for EC-based fenestration. These requirements are not easily compatible, and repeated insertion and extraction of large amounts of Li^+ ions lead to a gradual accumulation of Li^+-ions in the host material[12-15] (often referred to as "ion-trapping") with ensuing loss of EC performance. Removal of the trapped ions to re-gain the initial EC properties is essential for maintaining good device performance. It has been proposed that the host structure contains different types of intercalation sites:[13, 14] a network of connected sites with low inter-site barriers, which allows fast diffusion of the intercalated ions throughout the film, and other sites with high energy barriers which are able to trap the diffusing ions. It has been suggested by Bisquert[14, 15] that the high-energy barrier trapping sites can be filled by Li^+ ions having sufficient energy or by waiting for a long enough time.

We recently hypothesized that Li$^+$ ions could be de-trapped through the action of a high-enough energy or, alternatively, by waiting for a sufficient time. The former of these assumptions was experimentally verified[16], and we found that Li$^+$ ions could be extracted from the majority of the trapping sites (called "intermediate traps") under the action of an electrical current, whereas de-trapping was not possible from a minority of the sites (called "deep traps"). EC WO$_3$ films are typically operated in the potential range of 2.0–4.0 V vs. Li/Li$^+$, and the intermediate traps then yield a slow but persistent decline of the colored-state transmittance upon prolonged electrochemical cycling.[16] We discovered that the WO$_3$ films could regain their initial EC performance by the action of a weak current, $i.e.$, galvanostatic de-trapping of the accumulated Li$^+$ ions took place in the host.[16] This intriguing discovery, which may open avenues to maintain superior EC performance, has motivated us to carry out further work on ion trapping and de-trapping in WO$_3$ films.

Here we demonstrate that WO$_3$ thin films can repeatedly regain their initial EC performance by ion de-trapping so that $sustainable$ $rejuvenation$ is possible. Minor differences in charge capacity and de-trapping energetics observed after repeated rejuvenation do not significantly affect the EC performance. Furthermore, we show that de-trapping does not occur by simply waiting for a long-enough time, which points at the trapped Li$^+$ ions being "stable" and remaining strongly bound in the absence of an external stimulus.

The WO$_3$ films were deposited by magnetron sputtering onto glass per-coated with In$_2$O$_3$:Sn (known as ITO). Detailed preparation and characterization can be found in Supporting Information. We used cyclic voltammetry (CV) in the potential range of 2.0–4.0 V and at a scan rate of 20 mV s^{-1} to insert and extract Li$^+$ ions in ~300-nm-thick amorphous WO$_3$ films. All potentials were measured with regard to a Li/Li$^+$ electrode. Details are given in the Experimental Section. The area encircled by the CV curves represents the total stored charge capacity, which was calculated by integrating the insertion and extraction portions of the CV diagrams. Both charge capacity and optical modulation (at 550 nm) decreased upon

voltammetric cycling, as shown in Figure 1A and 1B. The first round of CV cycling was interrupted after 500 cycles, and it was found that the open circuit potential (OCP) had decreased from an initial value of ~3.27 to ~3.04 V (Figure 1C) because of charge accumulation in the film. A constant current density of ~3×10^{-6} A cm^{-2} was then applied for 20 h in the direction opposite to the one yielding Li$^+$ ion insertion in the host material with the aim of extracting the trapped Li$^+$ ions. The optical transmittance remained unaltered during the entire de-trapping procedure (Figure 1B and Figure S1), whereas the potential increased to ~5.8 V at the end of the process (Figure 1D) and then dropped to ~3.30 V during ~2 h after removing the constant current. The latter value is approximately the same as the initial OCP and suggests that the voltage decay caused by ion trapping[17] is regained.

In order to test whether the initial EC performance had been recovered or not, we performed a second round of CV cycling immediately after the first de-trapping process, again with 500 CV cycles. Optical modulation and charge capacity data confirmed that the EC properties of the degraded WO$_3$ film had been successfully re-gained and that it still displayed degradation features similar to the initial ones upon prolonged cycling (Figure 1A and 1B). A detailed comparison of CV curves is shown in Figure 2A and Figure S2 and demonstrates that the ion intercalation process is essentially the same after de-trapping as in the pristine film. The same constant current density was again applied for 20 h to refresh the film, and the OCP increased from 3.01 to 3.29 V after this second round of de-trapping (Figure 1C). A third round of CV cycling was conducted for 400 cycles and yielded substantially the same results as before. Then 800 cycles were used in the fourth round of CV cycling; it was found that the degradation features in the earlier part (up to ~500 cycles) were similar to those of the previous three rounds, and that reversible charge exchange as well as optical modulation declined at successively lower rates during the remaining 300 cycles (Figure 1A and 1B). After 800 CV cycles, the OCP had dropped from ~3.28 to ~2.90 V, which is a larger change than that for the initial three rounds of CV cycling (Figure 1C). Subsequent to the same de-

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trapping procedure as before, OCP returned to be 3.27 V and the EC performance was regained as proved by the fifth and final round of 500 CV cycles (Figure 1A and 1B). Figure 2B shows that the optical transmittance in the full range of visible light had recovered after the first de-trapping procedure, and further rounds of cycling and de-trapping yielded similar results. Furthermore, it is observed in Figure 1A and 1B that ion trapping degrades the optical transmittance predominantly in the colored state, whereas the bleached-state transmittance remains approximately the same throughout all cycles of ion trapping and rejuvenation (Figure 1A).

The details of the trapping and de-trapping/rejuvenation processes are still not accurately known, but a number of interesting observations can be made from the data presented here. Ion intercalation in EC materials takes place together with insertion of charge-balancing electrons from the outer electrical circuit, and the distribution of ion insertion potentials is known to be governed by the density of electronic states in the material.[18, 19] As apparent from the CV data in Figure 2A and Figure S3, Li^+ ion insertion and extraction initially take place in a wide potential range, specifically at 2.0–3.5 V, indicating a broad distribution of electronic energies in the host material. However, the high-potential limit for ion insertion and extraction shifts monotonically towards lower potentials upon extended cycling and, for example, Li^+ ion intercalation only occurs in the 2.0–3.0 V range after 500 CV cycles. This change of the CV curves is very similar to the change in the OCP (Figure 1C). The onset of ion intercalation is mainly governed by the position of the conduction band edge of WO_3 on the absolute electrochemical energy scale. The films are transparent in their bleached state irrespectively of the number of CV cycles, and hence we conclude that ion trapping and degradation are accompanied by a shift of the conduction band by ~0.3–0.5 eV towards higher energy. This shift may be due to an alteration of the ionization potential, which is known to be critically dependent on the atomic structure at the film surface.[20] Alternatively, irreversible ion trapping

may lead to the creation of new chemical species with molecular orbitals formed by removing states from the conduction band of WO_3.

It is also important to note that both inserted and extracted charge density decrease during extended cycling (Figure 1A). This indicates a more complex nature of the trap states than the one proposed by Bisquert;[13, 14] evidently there is a large number of available sites during the early cycles, and this number decreases during voltammetric cycling because of ion trapping. Hence the trapping process degrades the charge capacity because the trapped Li^+ ions block previously available intercalation sites. In earlier work[16] we suggested that the intermediate traps are associated with W^{4+} states, which are formed by the insertion of two Li^+ ions in the vicinity of the tungsten atom. This view may need some reconsideration in the light of the present experiments, however, and here we conjecture the following interpretation of the trap states: The reversible traps are associated with W^{5+} sites, each with a Li^+ ion bound to one of its adjacent oxygens, and the intermediate traps are subsequently formed from the reversible ones by insertion and bonding of another Li^+ ion. This is a relatively slow process because of the large activation energy, but over many cycles it leads to severe loss of charge capacity and optical modulation. Rejuvenation of the degraded films requires overcoming this activation energy, and therefore it can be accomplished only at high enough potentials (Figure 1D).

We demonstrated above that our de-trapping/rejuvenation procedure is sustainable and can be repeated several times with qualitatively similar behavior of charge capacity and optical modulation. However, closer scrutiny reveals significant differences between the rounds of degradation and rejuvenation and indicates that the material is not completely unaffected by the rejuvenation procedure. It is worth noting that, according to Figure 1A and 1B, both charge capacity and optical modulation degrade slightly faster for each round. In addition, the imbalance between inserted and extracted charge in each round of CV cycles, obtained from the difference between the first and last CV cycle (Figure 1A), shows a consistent increase; a major part of this effect appears to come from imbalance during the first

few cycles. There are also significant differences between the voltage curves taken during the rejuvenation process (Figure 1D) as well as in the OCP (Figure 1C). Specifically, there is a continuous shift towards lower potentials for both of these quantities in each round, which is most pronounced in the voltage *vs.* time curves. Figure 3 gives a more detailed picture of this latter effect and presents the derivative of the charge passing through the material during the rejuvenation process as a function of the potential. It is observed that the onset of the de-trapping/rejuvenation process exhibits a shift towards lower potentials of a magnitude that is similar to the change of the OCP.

The charge passing through the electrochemical cell during rejuvenation is probably composed of two parts: the Li^+ ions extracted from the WO_3 film and a second contribution due to side reactions in the electrolyte or at the solid–electrolyte interface. The estimated contribution of the de-trapped Li^+ ions is indicated by circles in Figure 3, and it is evident that this is only a small portion of the charge during rejuvenation. The flat portions of the voltage *vs.* time curves (Figure 1D), prevailing at long times, are almost certainly due to electrolyte decomposition,[21] but different processes may coexist at short times. The difference between the OCP and the onset voltage for charge extraction allows us to estimate activation energies in excess of 1.8 eV for the de-trapping process.

Apart from galvanostatic de-trapping, trapped Li^+ ions might be released by simply waiting for a sufficient time. In order to test this second possibility for Li^+ de-trapping, we first degraded a WO_3 film by running it through 500 CV cycles as before. The film was then left and its OCP was recorded. Both optical transmittance and OCP were barely altered during this process (Figure 4A, 4D and Figure S4A). A second round of 500 CV cycles was subsequently carried out, and it was found that the initial optical modulation and charge capacity were approximately the same at those at the last cycle for the first 500 CV cycles. This result suggests that Li^+ ions in intermediate traps are "stable" in the host material and cannot be released by long-time waiting. During the second round of 500 CV cycles, both

optical modulation and charge capacity continued to decline (Figure 4A and 4B), and the OCP decreased from 3.02 to 2.95 V. Detailed comparisons of CV data and optical spectra are presented in Figure 4C and Figure S4B, respectively. After 1,000 CV cycles (*i.e.*, the first 500 plus the second 500 cycles), galvanostatic de-trapping was conducted for 20 h to refresh the film. A third round of 500 CV cycles then clearly demonstrated that the film had regained its initial EC performance. Comparing the results of galvanostatic de-trapping and long-time waiting, one can therefore conclude that only the former approach plays a significant role in the rejuvenating process.

In a fixed potential range, the scan rate determines the amount of Li^+ ions that can be inserted, and a lower scan rate yields a larger amount of Li^+ insertion and more pronounced ion trapping, as shown in Figure S5. There seems to be a trade-off between scan rate and degree of ion-trapping on one hand and optical modulation on the other hand: lower (higher) scan rates result in higher (lower) degree of ion trapping but yield larger (smaller) optical modulation. Concerning EC devices, the amount of inserted Li^+ ions therefore should be controlled in order to optimize both cycle life and optical modulation.

In conclusion, ion-trapping is an intrinsic and inseparable part of ion-exchange processes and results in persistent degradation of the performance of EC devices. In the present work, we demonstrated that degraded WO_3 thin films can sustainably recover their initial EC performance, which is achieved by extracting the trapped Li^+ ions from the host WO_3. This rejuvenation process can be repeated many times. On the other hand, waiting for long times does not lead to extraction of the trapped Li^+ ions and thus fails to rejuvenate the WO_3 film. Our investigation clearly shows that ion trapping and rejuvenation are complicated processes and require further studies. These should encompass a variety of current densities and time spans, as well as potentiostatic measurements. It should also be noted that potential is high enough to activate electrochemical side reactions. Furthermore, we find some changes in the properties of the WO_3 films after multiple rejuvenations, but these changes do not seem to

affect the charge capacity and optical modulation significantly. The possibility to detrap Li^+ ions is of considerable interest for EC devices but may in practice necessitate the use of additional "dummy" layers serving as repositories for these ions. We finally note that our work may also have implications for batteries[22] and other types of ionics-based materials.

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Notes

The authors declare no competing financial interest.

References

(1)   Pacala, S.; Socolow, R. Stabilization Wedges: Solving the Climate Problem for the Next 50 Years with Current Technologies. *Science* **2004**, 305, 968-972.

(2)   UNEP, Buildings and Climate Change: Status, Challenges and Opportunities. *United Nations Environment Programme, Paris, France*, **2007**.

(3)   2011 Buildings Energy Data Book. *U.S. Department of Energy, Washington, DC* http://buildingsdatabook.eere.energy.gov/, **2012**.

(4)   Richter, B.; Goldston, D.; Crabtree, G.; Glicksman, L.; Goldstein, D.; Greene, D.; Kammen, D.; Levine, M.; Lubell, M.; Savitz, M.; Sperling, D.; Schlachter, F.; Scofield, J.; Dawson, J. How America Can Look within to Achieveenergy Security and Reduce Global Warming. *Rev. Mod. Phys.* **2008**, 80, S1-S109.

(5)   Granqvist, C. G. Electrochromic Materials: Out of a Niche. *Nat. Mater.* **2006**, **5**, 89-90.

(6)   Smith, G. B.; Granqvist, C. G. Green Nanotechnology: Solutions for Sustainability and Energy in the Built Environment. *CRC Press, Boca Raton, FL, USA,* **2010**.

(7)   Llordes, A.; Garcia, G.; Gazquez, J.; Milliron, D. J. Tunable Near-infrared and Visible Light Transmittance in Nanocrystal-in-glass Composites. *Nature* **2013**, 500, 323-326.

(8)   Clear, R. D.; Inkarojrit, V.; Lee, E. S. Subject Responses to Electrochromic Windows. *Energy Buildings* **2006**, 38, 758-779.

(9)   Fernandes, L. L.; Lee, E. S.; Ward, G. Lighting Energy Savings Potential of Split-pane Electrochromic Windows Controlled for Daylighting with Visual Comfort. *Energy Buildings* **2013**, 61, 8-20.

(10)   Granqvist, C. G. Electrochromics for Smart Windows: Oxide-based Thin Films and Devices. *Thin Solid Films* **2014**, 564, 1-38.

(11)   Granqvist, C. G. Handbook of Inorganic Electrochromic Materials. *Elsevier, Amsterdam, The Netherlands*, **1995**.

(12)   Bueno, P. R.; Faria, R. C.; Avellaneda, C. O.; Leite, E. R.; Bulhões, L. O. S. Li^+ Insertion into Pure and Doped Amorphous WO_3 films. Correlations between Coloration Kinetics, Charge and Mass Accumulation. *Solid State Ionics* **2003**, 158, 415-426.

(13)   Bisquert, J.; Vikhrenko, V. S. Analysis of the Kinetics of Lon Intercalation. Two State Model Describing the Coupling of Solid State Ion Diffusion and Ion Binding Processes. *Electrochim. Acta* **2002**, 47, 3977-3988.

(14)   Bisquert, J. Analysis of the Kinetics of Ion Intercalation: Ion Trapping Approach to Solid-state Relaxation Processes. *Electrochim. Acta* **2002**, 47, 2435–2449.

(15)   F. Fabregat-Santiago, G. Garcia-Belmonte, J. Bisquert, N. S. Ferriols, P. R. Bueno, E. Longo, J. S. Antónc, S. Castro-García, Dynamic Processes in the Coloration of WO_3 by Lithium Insertion, *J. Electrochem. Soc.* **2001**, 148, E302-E309.

(16)   Wen, R.-T.; Granqvist, C. G.; Niklasson, G. A. Eliminating Degradation and Uncovering Ion-trapping Dynamics in Electrochromic WO_3 Thin Films. *Nat. Mater.* **2015**, 14, 996-1001

(17)   M. Sathiya, A. M. Abakumov, D. Foix, G. Rousse, K. Ramesha, M. Saubanère, M. L. Doublet, H. Vezin, C. P. Laisa, A. S. Prakash, D. Gonbeau, G. VanTendeloo, J.-M. Tarascon, Origin of Voltage Decay in High-capacity Layered Oxide Electrodes. *Nat. Mater.* **2015**, 14, 230-238.

(18)   Niklasson, G. A. Electrochemical Measurements of the Electronic Density of States. *Phys. Scripta* **2015**, 90, 094005.

(19)   Strömme, M.; Ahuja, R.; Niklasson, G. A. New Probe of the Electronic Structure of Amorphous Materials. *Phys. Rev. Lett.* **2004**, 93, 206403.

(20)   Montero, J.; Guillén, C.; Granqvist, C. G.; Herrero, J.; Niklasson, G. A. Preferential Orientation and Surface Oxidation Control in Reactively Sputter Deposited Nanocrystalline SnO_2:Sb Films: Electrochemical and Optical Results. *ECS J. Solid State Sci. Technol.* **2014**, 3, N151-N153.

(21)   Ufheil, J.; Würsig, A.; Schneider, O. D.; Novák, P. Acetone as Oxidative Decomposition Product in Propylene Carbonate Containing Battery Electrolyte. *Electrochem. Comm.* **2005**, **7**, 1380-1384.

(22)   Xu, C.; Zeng, Y.; Rui, X.; Zhu, J.; Tan, H.; Guerrero, A.; Toribio, J.; Bisquert, J.; Garcia-Belmonte, G.; Yan, Q.; Amorphous Iron Oxyhydroxide Nanosheets: Synthesis, Li Storage, and Conversion Reaction Kinetics. *J. Phys. Chem. C* **2013**, 117, 17462 – 17469
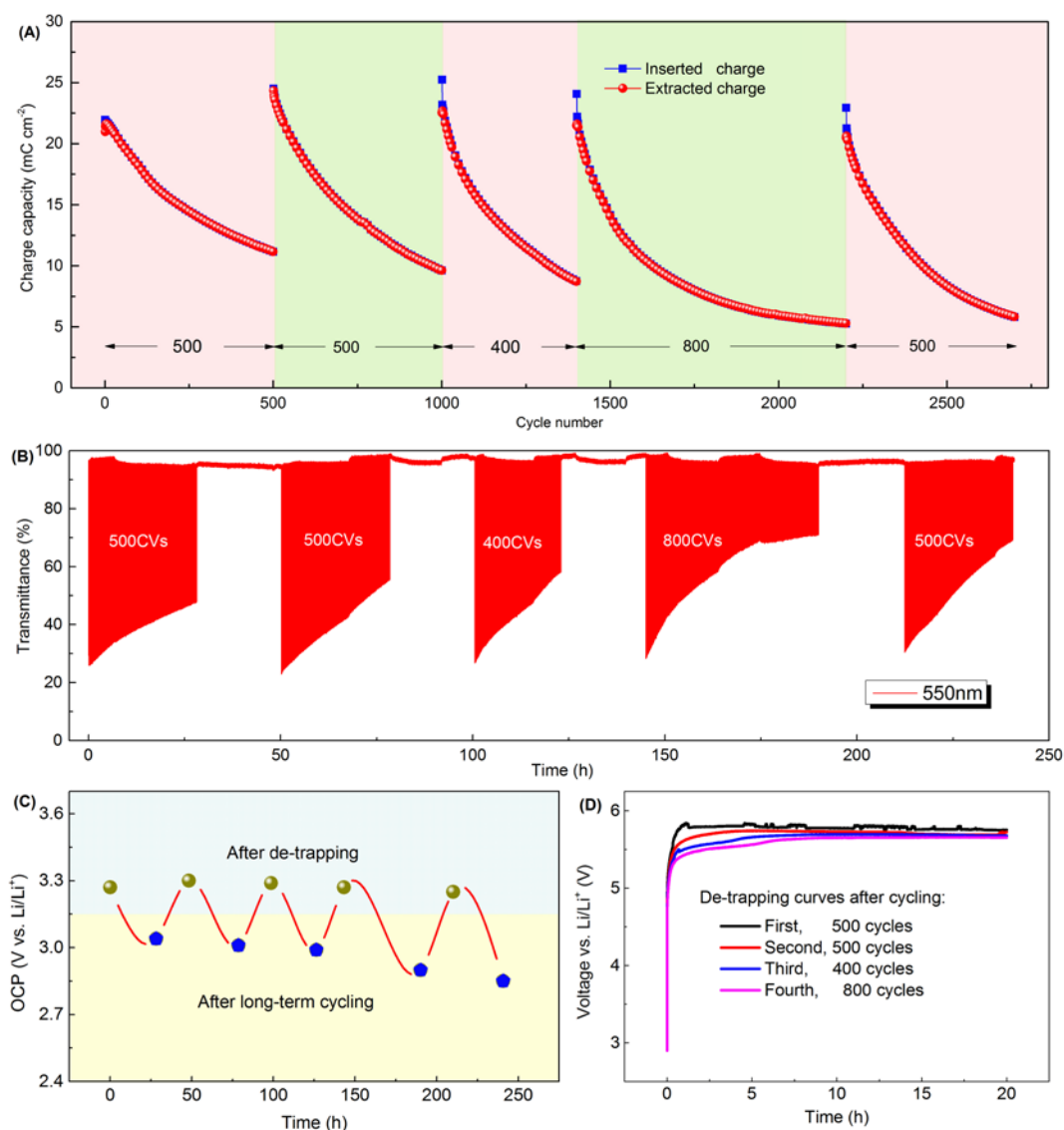
FIGURES

Figure 1. Repeated degradation and rejuvenation of the electrochromic performance for ~300-nm-thick WO$_3$ films. (**A**) Capacity for insertion and extraction of charge upon voltammetric cycling; ion de-trapping was conducted after the indicated numbers of cycles. (**B**) *In situ* optical transmittance of WO$_3$ films at a wavelength of 550 nm upon cycling in the range of 2.0–4.0 V *vs*. Li/Li$^+$ at a scan rate of 20 mV s^{-1}. (**C**) Open circuit potential (OCP) in initial state and after repeated degradation by long-term cycling and ion de-trapping by galvanostatic treatment. (**D**) Voltage *vs*. time galvanostatic rejuvenation after the indicated numbers of cycles; the current density was ~3 × 10^{-6} A cm^{-2}.
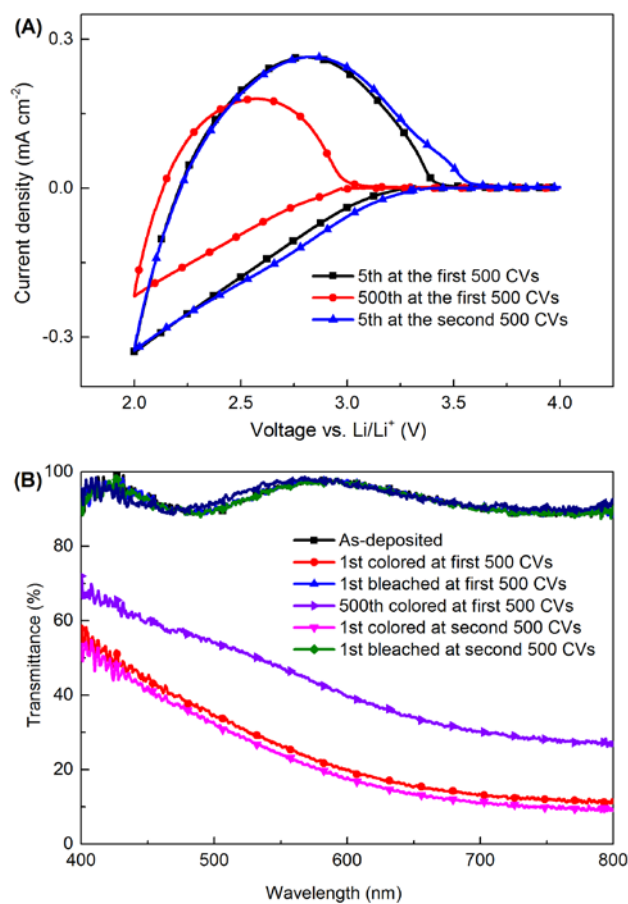
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Figure 2. (**A**) Cyclic voltammetry (CV) data for ~300-nm-thick WO_3 films recorded at different numbers of scans in the range of 2.0–4.0 V *vs*. Li/Li$^+$ at a rate of 20 mV s^{-1}. (**B**) *In situ* spectral optical transmittance for an as-deposited film and after the indicated number of CV cycles; bleached-state data overlap.
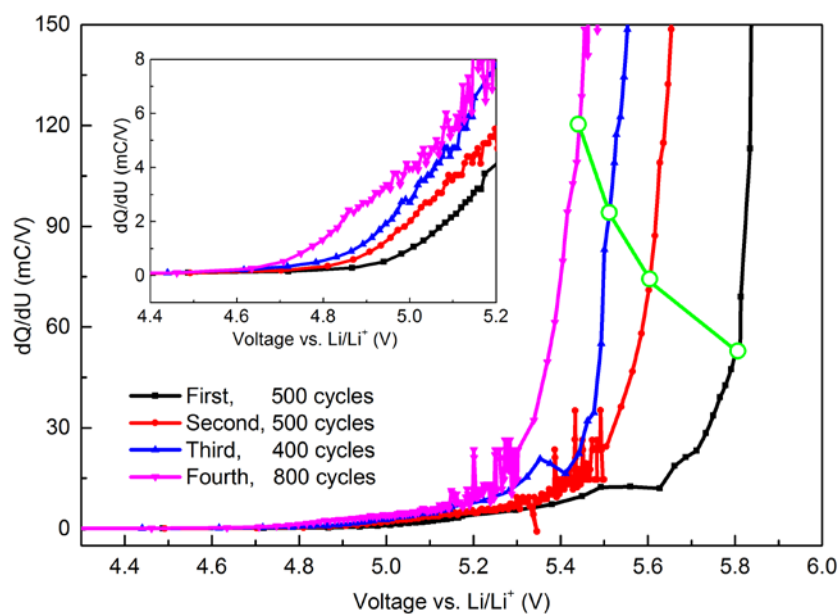
Figure 3. Derivative of extracted charge Q with respect to potential U for the WO_3 film earlier reported on in Figure 1. The inset is a close-up view of the low-potential range. Circles connected by straight lines indicate where the integrated charge under each curve becomes equal to the charge corresponding to Li^+ trapping, as obtained from the decrease in charge capacity during the course of the specified number of voltammetric cycles in Figure 1A
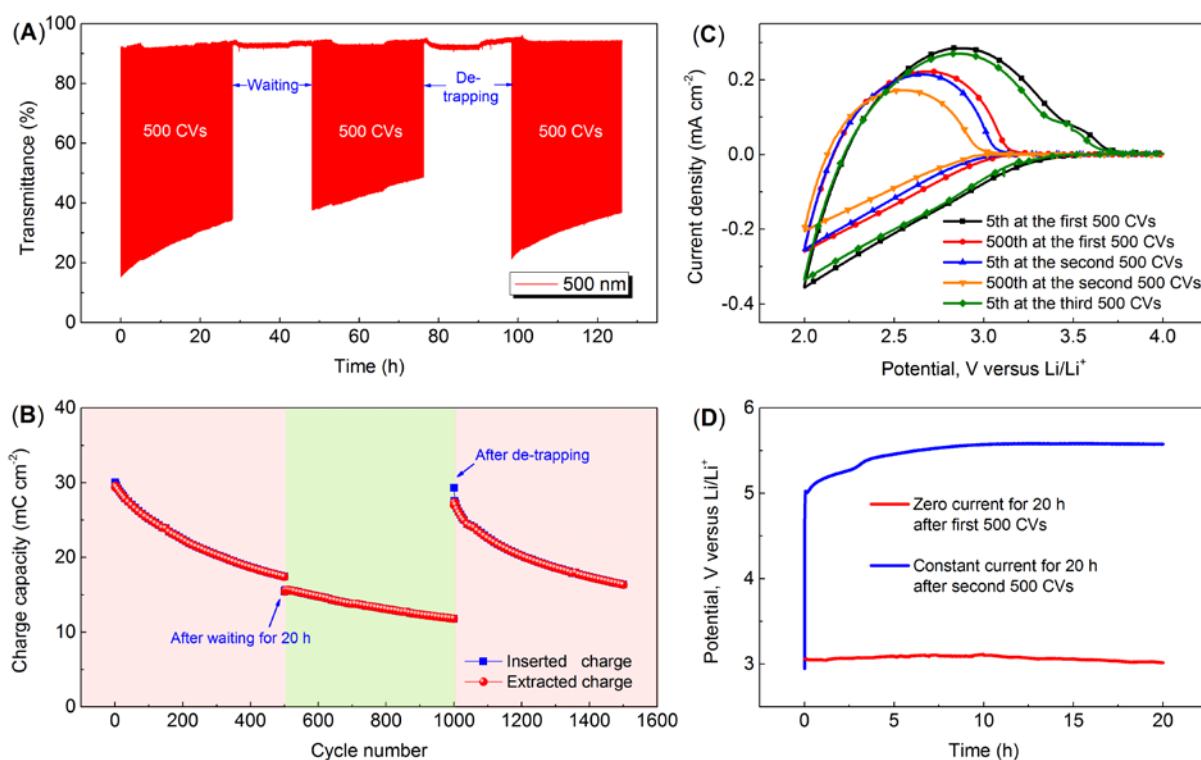
Figure 4. Performance of ~300-nm-thick WO$_3$ films during degradation by electrochemical cycling in the range of 2.0–4.0 V *vs*. Li/Li$^+$ at a rate of 20 mV s^{-1}, long-time immersion in electrolyte, and galvanostatic de-trapping. (**A**) *In situ* optical transmittance at a wavelength of 550 nm. (**B**) Charge capacity during voltammetric cycling. (**C**) CV data taken at the shown cycle numbers. (**D**) Open circuit potential at zero current and during ion de-trapping at a current density of ~3 × 10^{-6} A cm^{-2}.

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