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# Eliminating Electrochromic Degradation in Amorphous TiO$_2$ though Li-ion Detrapping

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**ABSTRACT**: The quest for superior and low-cost electrochromic (EC) thin films, for applications in smart windows, remains strong owing to their large importance for energy-efficient buildings. While the development of new EC materials for improved devices is important, diminishing or reversing degradation is another key issue, and electrical rejuvenation of degraded EC materials can offer new opportunities. Here we demonstrate that cathodically coloring EC thin films of TiO$_2$, which normally suffer from ion-trapping-induced degradation of charge capacity and optical modulation upon extensive electrochemical cycling, can recover their initial EC performance by a rejuvenation procedure involving Li$^+$ ion de-trapping. Thus the initial performance can be regained, and refreshed TiO$_2$ films exhibit the same degradation features as as-deposited films upon prolonged electrochemical cycling. The rejuvenation was carried out by using either galvanostatic or potentiostatic treatments. Our study may open avenues to explore the recovery not only of EC materials and devices based on those but also for other ion-exchange-based devices.

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Electrochromic (EC) thin films can regulate the amount of sunlight that passes through windows and glass facades and have a great potential for controlling solar heat gain and daylighting in energy-efficient buildings with good indoor comfort.[1,2] The standard large-area EC device embodies a W-oxide-based film separated from a Ni-oxide-based film by an electrolyte, and coloration and bleaching occur when ions are shuttled between these two films under the action of a voltage supplied to external transparent electrodes.[3-5] Moving charge from Ni oxide to W oxide makes them both dark, and reversing the charge transport bleaches them; hence oxides of Ni and W exhibit anodic and cathodic coloration, respectively. A critical requirement for the device is that the EC layers possess both high optical modulation and long-term durability under electrochemical cycling. Extensive work has been carried out to achieve this goal by searching for novel EC materials with superior performance. However, methods to reverse degradation and hence rejuvenate existing low-cost EC materials are equally important and have attracted interest only recently, especially with regard to galvanostatic ion de-trapping which was shown to be able to refresh degraded $WO_3$.[6-8]

Titanium dioxide, $TiO_2$, is an interesting alternative to the commonly used $WO_3$ as a cathodic EC material.[4,9] It is capable of going from optically transparent to deep blue by $Li^+$ ion insertion and returning to its transparent state by extraction of these ions; the optical modulation is associated with changes in the position of the Fermi level in the electronic density of states. The intercalation–deintercalation process in amorphous $TiO_2$ shows typical solid-solution behavior[10] and can be expressed, schematically, as[4]

$$TiO_2 + x(Li^+ + e^-) \leftrightarrow Li_xTiO_2,  \tag{1}$$

where $x$ is the amount of $Li^+$ intercalation and $e^-$ denotes charge-compensating electrons. In order to achieve high optical modulation, it is required that $x$ does not remain small in Eq. (1) which, in its turn, may be detrimental to device longevity. The failure to extract all of the

inserted ions in one electrochemical cycle leads to large amounts of Li$^+$ ions being accumulated in the host material over many cycles, as seen especially in battery-related studies.[10,11] Hence the reversible charge capacity is gradually decreased and results in degraded optical modulation. These results are consistent with recent reports that the sustained capacity loss upon electrochemical cycling is due to the incorporation of Li$^+$ ions in the host material,[11-14] thus pointing at an ion-trapping process which impedes subsequent ion insertion and erodes reversibility. Ion-trapping in a host material is a complex phenomenon and coupled to a variety of processes occurring in the solid state.[15-17] For lithium intercalation in metal oxides, a widely adopted picture considers two main limiting steps for the kinetics:[18] (*i*) the overcoming of a barrier at the ion injection interface (the electrolyte/TiO$_2$ interface), and (*ii*) diffusion of ions within the material. The latter process is the slower one. It has been proposed[15,17] that the host structure contains different types of intercalation sites: a network of shallow connected sites which allows fast distribution (low energy barrier, corresponding to reversible sites) of the intercalated ions throughout the film, and deep sites (high energy barrier, corresponding to traps) which immobilize the diffusing ions. The deep sites can be transitioned from reversible sites[15] and can be filled by Li$^+$ ions with high energy or by waiting for a sufficiently long time.[15,17] We hypothesize that the trapped ions could de-trap if they acquire large-enough energy to pass over the high-energy barrier. In fact, recent studies of ours found unambiguous evidence of ion trapping and de-trapping in the case of amorphous WO$_3$ (Ref. 7) and we demonstrated that, subsequent to a galvanostatic de-trapping process, the films could regain their initial EC performance sustainably.[6] This prior work motivated us to explore de-trapping phenomena in TiO$_2$ thin films.

In this paper, we present results on rejuvenation of degraded TiO$_2$ films by Li$^+$ ion de-trapping. We first studied *galvanostatic* de-trapping and show that the degraded TiO$_2$ electrode can be completely refreshed so as to recover its initial charge capacity and optical

modulation span. We found that ion de-trapping and electrolyte decomposition were indistinguishable phenomena during this de-trapping process. More importantly, we identify the driving force of the de-trapping by further investigation of the degraded $TiO_2$ films by *potentiostatic* de-trapping. Degraded $TiO_2$ films could also be recuperated by keeping them at a high-enough potential, thus leading to the conclusion that the potential is the key in order to overcome the energy barriers for the trapped ions in the host. Static relaxation of the trapped ions and effects of varying potential sweep rate and low-potential limit during electrochemical cycling are also discussed.

$TiO_2$ dioxide thin films with thicknesses of $250 \pm 20$ nm were deposited onto glass pre-coated with transparent and electrically conducting $In_2O_3$:Sn (*i.e.*, ITO) by use of reactive DC magnetron sputtering and were studied in an electrolyte of lithium perchlorate in propylene carbonate ($LiClO_4$–PC). The O/Ti atomic ratio was 2.0, as found from detailed analyses of similarly produced films by use of Rutherford Backscattering Spectrometry.[19] All potentials are given with $Li/Li^+$ as a reference. Experimental details can be found in the Supporting Information. The films were amorphous both in as-deposited state and after electrochemical treatments, as found by x-ray diffraction (Figure S1). Charge insertion and extraction were studied by cyclic voltammetry (CV) with simultaneous optical transmittance measurements. The depth profiles of the inserted ions are not known, but the fact that similarly prepared $TiO_2$ films displayed thickness-dependent electrochromism indicates that the ion density is highest in the outer part of the film.[20]

**Galvanostatic ion de-trapping**. Repeated $Li^+$ ion intercalation–deintercalation in $TiO_2$ films results in a modulation of their optical properties, and ion-trapping gradually erodes this EC performance. Figure 1a and 1b give an overview of the charge capacity and optical transmittance modulation at a mid-luminous wavelength $\lambda$ of 550 nm upon various treatments. The charge capacity was obtained from CV curves as described in the Methods section.
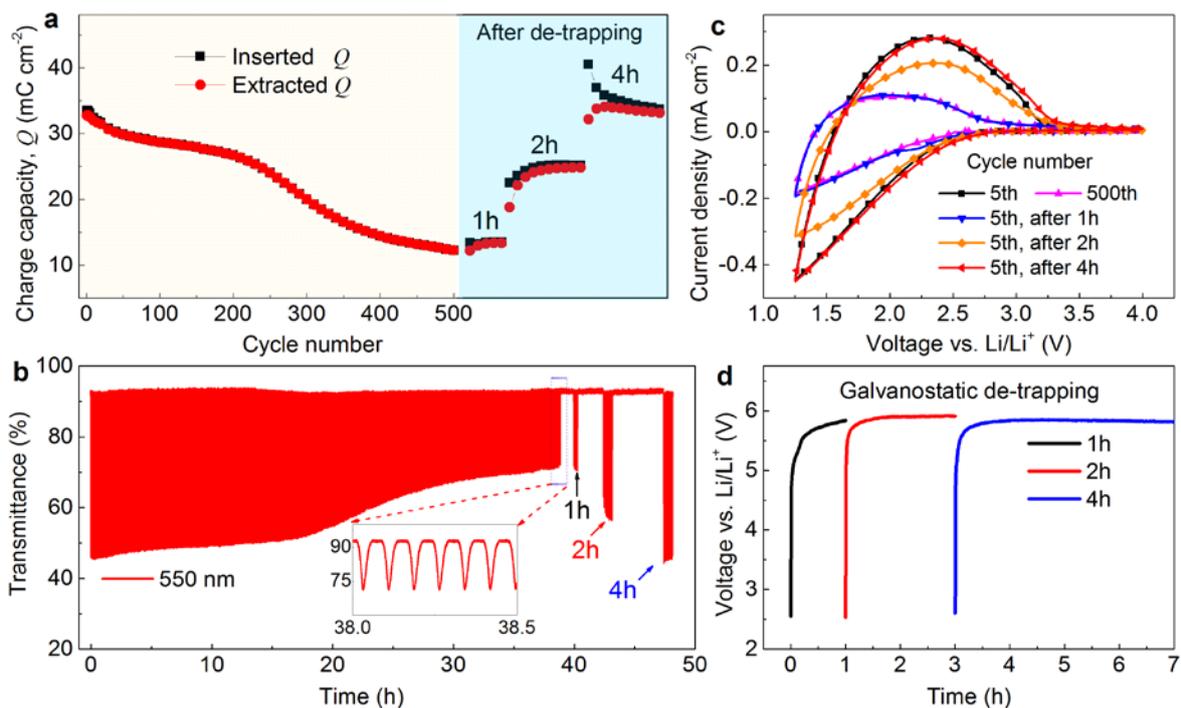
**Figure 1**. **Galvanostatic rejuvenation assessment of ~250-nm-thick TiO$_2$ films immersed in LiClO$_4$–PC.** (a) Charge capacity variation during CV cycling and subsequent galvanostatic de-trapping procedures; clear rejuvenation can be observed after ion de-trapping. The potential range was 1.25–4.0 V and the scan rate was 20 mV s$^{-1}$. (b) Corresponding *in situ* optical transmittance at $\lambda = 550$ nm. (c) CV data for various cycle numbers consistent with the sample treatments indicated in (a). (d) Voltage upon galvanostatic extraction of trapped ions; the current density was ~3 $\mu$A cm$^{-2}$.

CV data were first recorded for 500 cycles in the potential range of 1.25–4.0 V at a scan rate of 20 mV s$^{-1}$. The results (Figure 1a) show that the charge capacity is gradually decreased upon cycling and that there is a concomitant erosion of the optical transmittance modulation (Figure 1b). The decreased charge capacity is associated with ion trapping upon extensive CV cycling. Figure 1c shows that the CV response is severely curtailed after 500 CV cycles, and the open circuit potential (OCP) decreased from 3.1 to 2.5 V. The broad intercalation/de-intercalation features indicate a wide distribution of site energies, as expected in amorphous materials.[21] It is evident that the optical modulation degradation, induced by the decreased

reversible charge capacity, only appears as a decline of the colored state whereas the bleached state remains essentially intact (Figure 1b). When ions are inserted into the $TiO_2$ matrix, optical absorption ensues as a result of charge-compensating electrons from the external circuit, which are concurrently injected to fill the conduction band. Hence, the Fermi level shifts towards larger energies in the density of states; conversely, optical transparency is regained when electrons are extracted and the position of the Fermi level returns to below the conduction band. When ion trapping takes place, we surmise that the charge-compensating electrons associated with the trapped ions fill band-gap electronic states[15,22,23] rather than the conduction band; thus the bleached state is not expected to be affected by ion trapping.

The trapping sites can be of two kinds: (*i*) already existing in the disordered system, or (*ii*) formed from reversible sites.[15] The second case appears to be dominating, and once a $Li^+$ ion is trapped it blocks at least one reversible site. This mechanism will gradually decrease the amount of reversible sites upon CV cycling and therefore progressively lead to a degradation of the colored state. The detailed trapping mechanism is not yet clear, but it is interesting to note that trapped $Li^+$ ions may bind to oxygen to form irreversible $Li_2O$ complexes during intercalation,[10,24,25] which hence could be a reason for decreased reversible charge capacity.

Galvanostatic de-trapping was conducted with the aim to extract the trapped $Li^+$ ions (Figure 1d, black curve) and can be understood as a transformation of the irreversible sites to reversible ones. A constant current density of ~3 $\mu A\ cm^{-2}$ was applied to the $TiO_2$ electrode for one hour, and the potential increased from the initial ~2.5 V to 5.7 V. CV cycling was then performed for five cycles, which led to some very slight recovery of charge capacity and optical modulation. The same de-trapping procedure was executed for another two hours (Figure 1d, red curve) and was followed by 10 CV cycles. The charge capacity and optical modulation were partly recovered but still lay far from the initial values. A third round of CV cycling for another 4 h (Figure 1d, blue curve) was then employed, and the EC performance

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was totally regained (Figure 1a, 1b, and 1c). After each de-trapping procedure, one can observe a relatively large charge density imbalance during the first few CV cycles, which may be due to the formation of a new solid–electrolyte interface,[26,27] Li depletion in the near-surface region,[10] or a combination of these. From these results one can conclude that galvanostatic de-trapping for seven hours (1 + 2 + 4 h) is enough to refresh the degraded $TiO_2$ electrode. Generally speaking, it is desirable to regain the initial EC performance in as short a time as possible, since the high potential (~5.7 V) may lead to a decomposition of the electrolyte[28] during the de-trapping process. The potential was seen to rapidly reach ~5.7 V during the de-trapping process, and it remained there during the full duration of the galvanostatic treatment. The potential did not vary even after the ions had been totally de-trapped, which took a maximum of seven hours, as shown by extending the galvanostatic treatment to 20 h (Figure S2). Thus it can be concluded that $Li^+$ ion de-trapping and electrolyte decomposition cannot be distinguished in this process.

It is also interesting to note that the optical transmittance remained unchanged during the entire de-trapping process (Figure 1b and Figure S3) and the OCP returns to its initial value after de-trapping thus suggesting that the voltage change caused by ion trapping is eliminated. X-ray diffraction measurements showed that $TiO_2$ maintained its amorphous character after severe degradation by CV cycling as well as after rejuvenation (Figure S1). Furthermore, the refreshed electrode still followed the same degradation behavior as in the initial film upon prolonged CV cycling thereby indicating that the initial EC performance can be sustainably regained (Figure S3). The refreshment of the optical transmittance is effective in the full spectral range for visible light ($380 < \lambda < 700$ nm), as illustrated in Figure S4; this recovery is complete, which is at variance with the case of $WO_3$ in which a small fraction of $Li^+$ ions was permanently trapped.[6]

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**Potentiostatic ion de-trapping.** Potentiostatic de-trapping can serve as a valuable alternative to galvanostatic treatment and might offer ways to decouple ion de-trapping from side reactions in the electrolyte by fine-tuning the applied potential. To this end, we first subjected a $TiO_2$ thin film to 500 CV cycles in the range of 1.25–4.0 V so that severe ion trapping was induced, as apparent from Figure 2a and 2b. The degraded electrode was then kept at 4.0 V for 2 h, and subsequent CV cycling did not give any evidence for recovery of the charge capacity. Repeated treatment at 4.0 V for 2 h yielded identical results and clearly showed that a potential of 4.0 V is too low to de-trap the ions. It has been reported[28] that propylene carbonate, which is present in our electrolyte, begins to decompose when the upper potential limit exceeds 4.5 V, and therefore it is essential to explore whether the degraded $TiO_2$ can be refreshed when the potential is equal to or less than this threshold value. We noted that charge capacity and optical modulation were barely improved after the degraded $TiO_2$ was kept at 4.5 V for 4 h (Figure 2). As seen in Figure 2d, the current upon potentiostatic treatment at 4.0 V and 4.5 V is as low as ~0.05 $\mu$A cm$^{-2}$, *i.e.*, charge exchange is almost nil in this potential region. Since the potential rapidly reached 5.7 V in the earlier experiments on galvanostatic de-trapping, the $TiO_2$ film was next kept at 5.7 V for 7 h and it was noted that the current passing the electrode was much larger than in the former potentiostatic recordings at lower voltages; specifically the current density was 3–5 $\mu$A cm$^{-2}$ (Figure 2d, violet curve). Subsequent to this treatment, the degraded $TiO_2$ thin film regained its initial charge capacity and optical modulation (Figure 2). It is worth noting that, in the galvanostatic de-trapping, a current density of ~1 $\mu$A cm$^{-2}$ or more could successfully refresh the degraded electrode and that the corresponding potential spontaneously reached ~5.7 V whereas, in the potentiostatic de-trapping, a current density of ~0.01 $\mu$A cm$^{-2}$ failed to refresh the film. However, keeping the potential at 5.7 V during potentiostatic refreshment yielded a

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current density of ~3 $\mu$A cm$^{-2}$, *i.e.*, the same current density as in our galvanostatic de-trapping experiment.
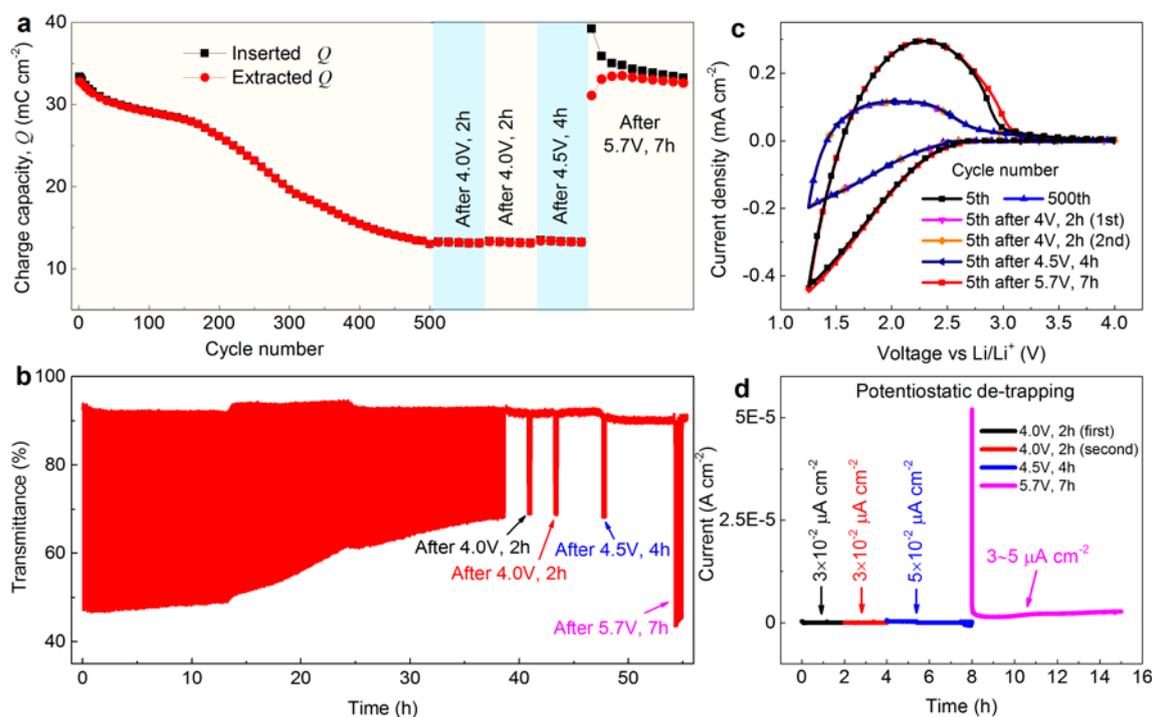


**Figure 2. Potentiostatic rejuvenation assessment of ~250-nm-thick TiO$_2$ films immersed in LiClO$_4$–PC.** (a) Charge capacity variation during CV cycling and subsequent potentiostatic de-trapping procedures; the potential range was 1.25–4.0 V and the scan rate was 20 mV s$^{-1}$. (b) Corresponding *in situ* optical transmittance at $\lambda$ = 550 nm. (c) CV data for various cycle numbers consistent with the sample treatments indicated in (a); overlapping CV data were found for the 500th cycle, the 5th cycle after the first and second 2-h periods at 4.0 V, and the 5th cycle after 4 h at 4.5 V. (d) Current density upon extraction of trapped ions.

**Static relaxation.** The next question to be explored concerns static relaxation: whether the trapped ions are stable in the host of TiO$_2$. To probe this issue, TiO$_2$ films were CV treated as described above for 500 cycles in order to ensure a high degree of Li$^+$ incorporation, and the films were then left electrically disconnected for 20 h (Figure 3). Both optical transmittance and OCP were seen to remain almost unaltered during this resting process (Figure S5 and

Figure 3, inset). The samples were subsequently exposed to a second round of 300 CV cycles, and it was found that the optical modulation interval and charge capacity had recovered only marginally compared with the situation prior to the resting. The miniscule boost in charge capacity and optical modulation after the resting period may be due to a very small fraction of trapped ions having been spontaneously released so that they reside inside the host material rather than diffuse back into the electrolyte. This notion is supported by the observation that the OCP does not change during 20 h of sample resting (Figure 3, inset). In other words, some irreversible sites seem to transform to reversible sites in the host structure;[15] however, this fraction is negligible compared with the ion densities involved in the rejuvenations accomplished by either galvanostatic or potentiostatic de-trapping. After the 800 (*i.e.*, 500 + 300) CV cycles, potentiostatic de-trapping at 5.7 V for 7 h was adopted to refresh the degraded $TiO_2$ film. Prolonged CV cyclings showed that the EC performance was now regained and still displayed the same degradation features as in the initial round of CV cycling (Figure 3 and Figure S5).
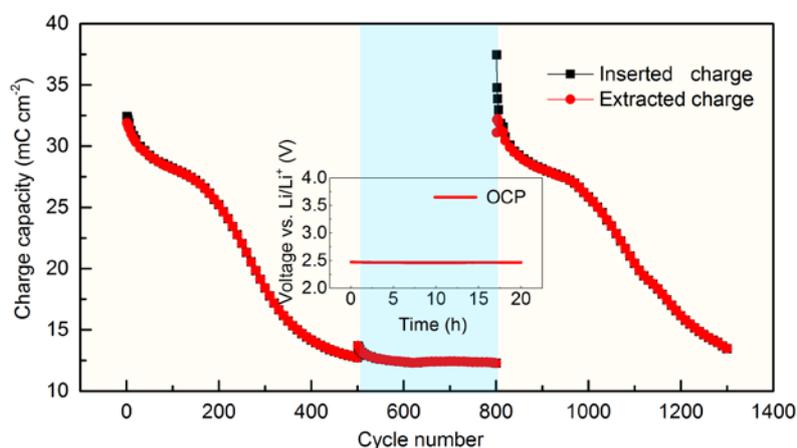


**Figure 3**. **Degradation behavior of ~250-nm-thick $TiO_2$ films immersed in $LiClO_4$–PC.** A film was first subjected to 500 CV cycles for a potential range of 1.25–4.0 V at a scan rate of 20 mV s$^{-1}$ and was then rested for 20 h. This film was then subjected to 300 analogous CV cycle, and the film was subsequently exposed to potentiostatic de-trapping at 5.7 V for 7 h. A final round of 500 CV cycles proved that the film was refreshed after the ion de-trapping.

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**The roles of potential scan rate and lower cut-off potential.** We now consider EC devices which, in general, demand fast coloration dynamics and large optical modulation. **Figure 4**a shows CV data recorded for the potential window 1.25–4.0 V in the $0.1 \leq s \leq 100$ mV s$^{-1}$ range of scan rates. Most of the charge exchange occurs below 3.5 V, and no evidence can be seen for electrolyte decomposition even at the lowest potentials and scan rates. The results clearly show that the charge capacity and optical modulation are strongly dependent on scan rate, and lower values of $s$ yield larger charge capacity and optical modulation span (Figure 4b and Figure S6). As presented in Figure 4a, the charge exchange takes place in a broad potential range and no sharp peaks can be discerned even at 0.1 mV s$^{-1}$—*i.e.*, during 15 h for one CV cycle and giving ample time for diffusion of Li$^{+}$ in the host—thus confirming solid-solution formation for Li$^{+}$ intercalation in amorphous TiO$_2$. This behavior is principally different from that of crystalline TiO$_2$ for which Li$^{+}$ intercalation/de-intercalation is a phase transformation process.[27, 29] Expectedly, a lower scan rate allows a larger amount of Li$^{+}$ ions to enter the host structure. This insertion is associated with unambiguous evidence for ion trapping (for example at $s \leq 20$ mV s$^{-1}$) although the maximum charge capacity clearly has not been reached (Figure 4b).

Except by lowering the scan rate, charge exchange can be enhanced by extending the lower limit $U_L$ of the potential window for the CV scans (Figure 4c), and this extension also yields larger optical modulation (Figure 4d and Figure S7). However, a lower $U_L$ seems to lead to a more pronounced ion-trapping effect since a larger charge imbalance is observed when $U_L$ was decreased to 1.0 V (Figure 4c, inset); moreover, electrochemical side reactions[14,30] were apparent at $U_L = 1.0$ V when the scan rate was very low (Figure S8). Long-term CV cycling was conducted on TiO$_2$ films in the range of 1.0–4.0 V, and galvanostatic detrapping was then performed to refresh the electrode. However, restoration of charge capacity was not better

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than to ~50% of the initial value, and pronounced imbalance between inserted and extracted charge density was apparent as CV scanning was resumed after the galvanostatic treatment (Figure S9). Clearly, rejuvenation of the EC performance was incomplete, and the electrode showed faster degradation than before during prolonged CV cycling presumably as a consequence of irreversible formation of Li–Ti oxide compounds.[30]
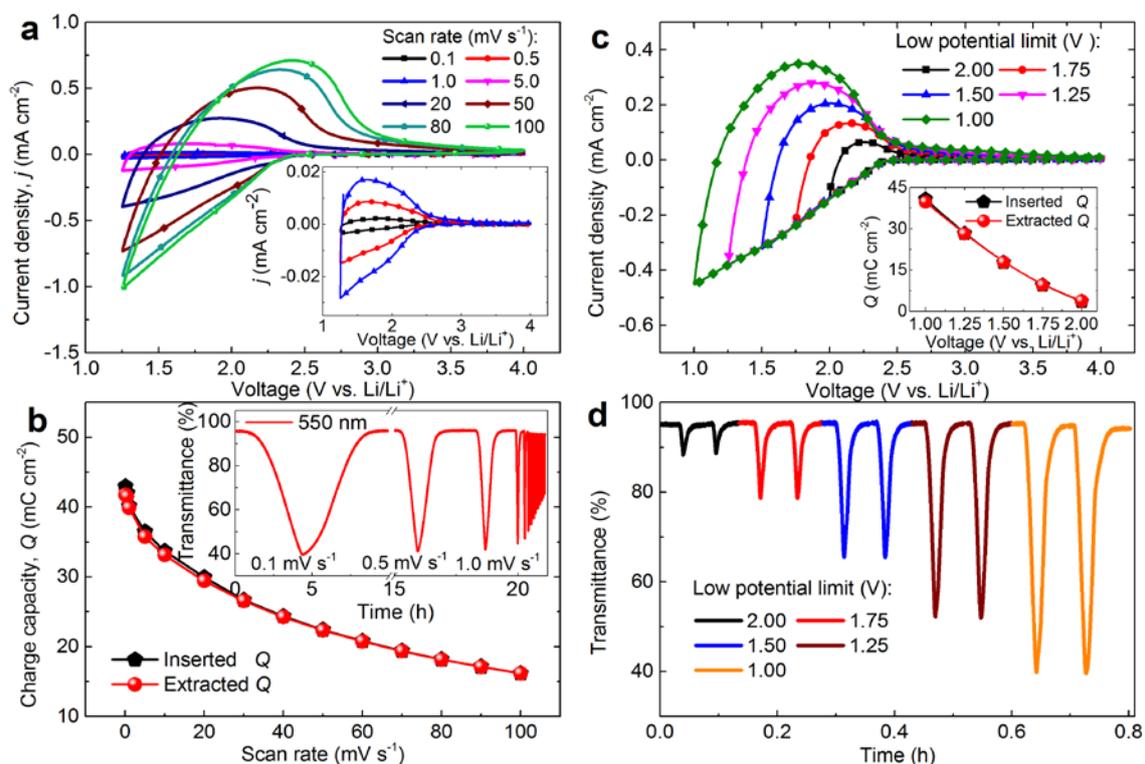


**Figure 4**. **Electrochromic performance of ~250-nm-thick TiO$_2$ films immersed in LiClO$_4$–PC, with consideration of voltage scan rate and potential interval.** (a) Cyclic voltammograms taken at various scan rates for a potential window of 1.25–4.0 V; inset shows data on an expanded scale for current density. (b) Charge capacity at different scan rates; inset shows optical transmittance at $\lambda = 550$ nm for decreasing scan rate. (c) Cyclic voltammograms for potential windows defined by an upper limit of 4.0 V and various lower limits; inset shows charge capacity for the corresponding potential windows. (d) Optical transmittance at $\lambda = 550$ nm for the same potential windows as in (c); two CV scans were conducted for each potential window.

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We conclude that $Li^+$ ion intercalation/de-intercalation in amorphous $TiO_2$ thin films is a solid solution process, and ion-trapping is a quintessential and inseparable part of the charge exchange process which results in persistent degradation of the films' charge capacity and optical properties. More importantly, the degraded films, after de-trapping by either galvanostatic or potentiostatic treatments, are able to provide rejuvenated electrochromic performance. The present work on amorphous $TiO_2$ thin films, in conjunction with the rejuvenation concept for refreshing electrochromism, is potentially promising for low-cost, long-cycle-life electrochromics-based light-transmitting and light-reflecting devices. Furthermore, ion trapping is a ubiquitous phenomenon, and our current work may also have implications for developing and deploying other ion-exchange-based devices such as batteries.

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