Electrochromic Batteries *Hot Paper*

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Trace H_2O_2-Assisted High-Capacity Tungsten Oxide Electrochromic Batteries with Ultrafast Charging in Seconds

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Abstract: *A recent technological trend in the field of electrochemical energy storage is to integrate energy storage and electrochromism functions in one smart device, which can establish efficient user–device interactions based on a friendly human-readable output. This type of newly born energy storage technology has drawn tremendous attention. However, there is still plenty of room for technological and material innovation, which would allow advancement of the research field. A prototype Al-tungsten oxide electrochromic battery with interactive color-changing behavior is reported. With the assistance of trace amount of* H_2O_2, *the battery exhibits a specific capacity almost seven times that for the reported electrochromic batteries, up to 429 mAh* g^{-1}. *Fast decoloration of the reduced tungsten oxide affords a very quick charging time of only eight seconds, which possibly comes from an intricate combination of structure and valence state changes of tungsten oxide. This unique combination of features may further advance the development of smart energy storage devices with suitability for user–device interactions.*

Electric energy storage systems, such as batteries and supercapacitors, which are able to store electrical energy in a chemical form and release it whenever needed, are a fundamental building block of modern life.[1] Such systems can mitigate energy shortages and global climate warming issues that the world is currently facing.[2,3] Thus, in the past decade, great efforts have been made to build better energy storage systems with higher power, higher energy, and longer life spans.[4–9] While much of the previous work focuses on optimizing the performance of energy storage systems, a number of novel devices have been realized that retain the "primary function" of energy storage systems (that is, energy storage and release on demand), and also incorporate new functionality to create novel types of multifunctional energy storage systems (for example, the smart energy storage system).[10–12] As a matter of fact, recent pioneering works have enabled successful fabrication of smart energy storage devices by incorporating electrochromic materials into electrodes inside energy storage devices, in which electrode color or transmittance reversibly changes in response to an applied voltage. For example, by creating a supercapacitor electrode with a pattern composed of electrochromic $W_{18}O_{49}$ nanowires on a polyaniline background, we have demonstrated a smart supercapacitor in which the level of energy stored can be constantly and visually conveyed through recognizing variations in pattern color schemes during the capacitive process.[13] A type of self-rechargeable electrochromic battery using electrochromic Prussian blue as the electrode material was recently reported, and the discharging/charging of the electrochromic battery corresponds to its bleaching/coloration.[14] Clearly, such devices enable a highly desired and convenient user–device interface based on a friendly human-readable output. However, the field is still rather young and many unsolved problems exist. For example, the specific capacity that the electrochromic battery delivers is rather low, 63.6 mAh g^{-1}, and the battery device needs a very long time for self-charging (12 hours).[10] Therefore, exploring smart electrochromic batteries with high performances is a worthwhile field of inquiry, and various solutions for building electrochromic batteries with new device configurations are eagerly sought.

It is well-known that electron transfer can take place between two materials with different work functions when they are put in contact or connected with a metal wire. When a selected material is put in contact with an electrochromic material (for example tungsten oxide and Prussian blue) the resulting electron transfer gives rise to an electrical current that exhibits battery-like characteristics. In the meantime the transferred electrons induce coloration of the electrochromic material, enabling devices to function with intelligible, interactive modes. On the basis of the above considerations, we selected an aluminum (Al)/tungsten oxide system upon which to build new electrochromic batteries. The work function difference, or driving force for coloration of the Al/tungsten oxide system, is large (1.96 eV; Figure 1 a).[15] A schematic of a typical Al/tungsten oxide electrochromic battery is given in Figure 1 b. In the discharging process, Al can be oxidized and releases electrons to form Al^{3+} ions, based on Reaction (1), whereas tungsten oxide (herein, we use $W_{18}O_{49}$ or $WO_{2.72}$) can act as an oxidant to acquire electrons by the reduction of W^{6+} to W^{5+}, W^{4+}, or even W^{3+},

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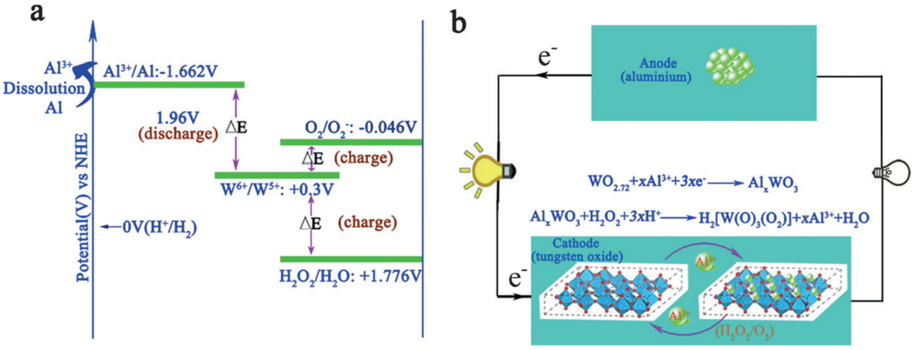

Figure 1. a) Energy level transition diagram of the battery anode and cathode material of the Al-tungsten oxide electrochromic battery, showing a big voltage drop from Al to tungsten oxide, as well as H_2O_2 to tungsten oxide. Three methods may be used to charge the battery: oxygen in air, an external current, or H_2O_2 (along with the redox couple $H_2O_2(O_2)$ to $H_2O(O_2^-)$. b) An LED connected to the battery is illuminated upon electron transfer and Al^{3+} insertion, and vice versa.

according to Reaction (2). This step is accompanied by the insertion of charge-balancing ions (Al^{3+}, Mg^{2+}, Na^+, K^+, Li^+) derived from the electrolyte when tungsten oxide and Al electrodes are connected, which also cause the electrode to change color from transparent to blue. For the charging process, reduced blue tungsten oxide is oxidized by oxygen molecules in air or by other oxidants (Reaction (3)), returning the metal oxide to its initial transparent state. However, the rate of charge transfer from the reduced blue tungsten oxide to oxygen molecules is very slow because of low conduction band level of the metal oxide (Figure 1a), resulting in long charging times when the battery requires spontaneous recharging using the oxygen in air. To this end, we propose the addition of a small amount of exogenous H_2O_2 as a new charging strategy for the Al/tungsten oxide electrochromic battery, with an intent to accelerate the oxidation reaction of the reduced blue tungsten oxide (Reaction (4)), and consequently decrease the charging time substantially. Another benefit from the addition of H_2O_2 is that “deep” active sites in tungsten oxide that are difficult to access may be activated by H_2O_2, which would give enlarged storage capacity.[16]

$$\mathrm{Al} \rightarrow \mathrm{Al}^{3+} + 3\,\mathrm{e}^- \tag{1}$$

$$\mathrm{WO}_{2.72} + x\,\mathrm{Al}^{3+} + 3\,x\mathrm{e}^- \rightarrow \mathrm{Al}_x\mathrm{WO}_3 \tag{2}$$

$$\mathrm{Al}_x\mathrm{WO}_3 + \mathrm{O}_2 \rightarrow \mathrm{WO}_y + x\,\mathrm{Al}^{3+} + \mathrm{O}^{2-} \tag{3}$$

$$\mathrm{Al}_x\mathrm{WO}_3 + \mathrm{H}_2\mathrm{O}_2 \rightarrow \mathrm{H}_2[\mathrm{W(O)}_3(\mathrm{O}_2)] + x\,\mathrm{Al}^{3+} + 3\,x\mathrm{OH}^- \tag{4}$$

$$\mathrm{H}_2[\mathrm{W(O)}_3(\mathrm{O}_2)] + y\,\mathrm{e}^- + x\,\mathrm{Al}^{3+} \rightarrow \mathrm{Al}_x\mathrm{WO}_3 + \mathrm{OH}^- \tag{5}$$

Following this concept, we demonstrate a trace H_2O_2-assisted Al-tungsten oxide electrochromic battery with interactive color-changing behaviors. The battery exhibits a high specific capacity up to 429 mAh g^{-1}, which is much larger than that for the reported electrochromic batteries. The addition of trace H_2O_2 was found to enable fast decoloration of the reduced tungsten oxide, thus affording a very quick charging time of only eight seconds.

$W_{18}O_{49}$ nanowire, a form of tungsten oxide nanomaterial, was used as a battery active material in this work because it exhibits a reversible color switch upon insertion or extraction of ions (induced by discharging and charging), presenting as blue in the colored state or colorless in the bleached state. Briefly, $W_{18}O_{49}$ nanowires were grown on an FTO-coated glass substrate using a previously reported approach; WCl_6 was dissolved in ethanol, followed by a hydrothermal reaction at 180 °C for 12 h and subsequent annealing at 200 °C in an argon atmosphere to achieve close contact at the interface.[17] Detailed information about the synthesis and characterization of $W_{18}O_{49}$ nanowires is provided in the Supporting Information. The as-prepared Al-tungsten oxide electrochromic battery is shown in Figure 2a. This unique battery is composed of a $W_{18}O_{49}$ nanowire film deposited on a piece of FTO glass, a strip of aluminum foil attached onto one side of another piece of FTO glass, and an aqueous electrolyte (or even pure water) in between containing Li^+, K^+, Na^+, Mg^{2+}, or Al^{3+}. Interestingly, in such a battery configuration even pure water permits the electrochromic batteries to work well, although pure water itself does not conduct ions very effectively. The main reason for this may be that Al^{3+} ions enter the system when Al foil is oxidized to Al^{3+} during the discharging process, based on Reaction (1), thereby increasing the conductivity of the electrolyte solution.

An interesting function of the Al-tungsten oxide battery is that it displays changes in color in response to varying levels of stored energy. As shown in Figure 2a, the as-prepared battery thin film is transparent, which is indicative of a fully charged battery state. This state is apparent when a red light-emitting diode (LED) is connected to the Al-tungsten oxide battery with a copper wire (Figure 2b), causing the LED to glow at its brightest. Once the hue of the battery thin film changes to deep blue, the LED no longer lights up (Figure 2c), implying that the battery is exhausted. After storing of the exhausted battery for 24 hours in air, it spontaneously returned to a light blue color. The decoloration of the battery from deep to light blue corresponds to the charging process of the battery (Reaction (3)). Subsequently, it was possible to light up the LED using the self-recharging battery (Figure 2d). However, to fully charge the Al-tungsten oxide battery in this way, the battery must be left in air for a very long time (at least 24 hours), and the intensity of light produced from the recharged battery is rather dim. In contrast, after addition of a small amount of H_2O_2 (1 mL, 30 %) the Al-tungsten oxide battery was charged up in several seconds and emitted a very bright light (Figure 2e), offering a decisive advantage over other electrochromic batteries (a video for the quick charging of the battery is available in the Supporting Information). The chromic behavior of the

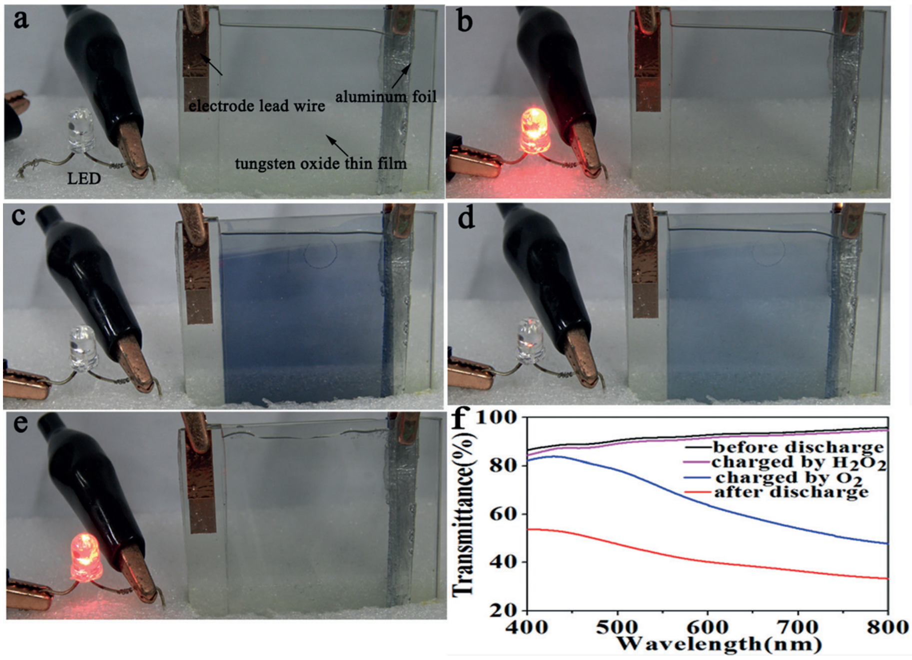

Figure 2. a) The as-prepared battery in a fully charged state appears transparent. LED not connected. b) An LED lights up brightly upon connection of Al and tungsten oxide electrodes through a copper wire. c) The LED does not light up when the battery thin film is deep blue in color after 24 h. d) The LED is lit up again after standing in air for 24 h. e) The Al-tungsten oxide battery charges up in just several seconds after injection of a small amount of H_2O_2. f) The Al-tungsten oxide battery regenerated by H_2O_2 under charged conditions typically manifests higher light transmittance in the whole visible range (400–800 nm), when compared to the battery under discharged conditions, or charged/discharged batteries regenerated by oxygen.

Al-tungsten oxide battery can also be monitored by in situ UV/Vis spectroscopy. The Al-tungsten oxide battery regenerated by H_2O_2 under charged conditions typically manifests higher light transmittance in the whole visible range (400–800 nm), when compared to the battery under discharged conditions, or charged/discharged batteries regenerated by oxygen (Figure 2 f). For the battery charged by oxygen, the transmittance at 633 nm during charging is increased by about 60 % after a long recovery time of 24 h, showing a rather slow charging or decoloration. On the contrary, for the battery charged by H_2O_2, the transmittance increased to 92 % very quickly, indicating that H_2O_2 can greatly accelerate the charging or decoloration rate of the Al-tungsten oxide battery.

The battery characteristics of the Al-tungsten oxide electrochromic battery using an electrolyte containing Al^{3+} ions was further characterized with an electrochemical workstation. The assembled battery shows an open-circuit potential (OCP) of about 1.2 V, lower than the theoretical potential (1.96 V) because of polarization and resistance losses (voltage drop upon discharge onset (IR drop)) of the battery, but much higher than that of the previously reported Prussian blue electrochromic batteries (0.4 V).[14] Figure 3 a presents a typical cyclic voltammetry (CV) curve derived from the two-electrode Al-tungsten oxide battery in aqueous $AlCl_3$ (1 M) between 0–1.2 V, in which a $W_{18}O_{49}$ film on FTO is used as the working electrode and Al foil serves as both the counter electrode and the reference electrode. A cathodic and anodic peak are discerned at the potentials of 0.15 and 0.5 V, respectively, which can be attributed to movement of ionic species into or out of the tungsten oxide matrix during the charge/discharge process. For our Al-tungsten oxide electrochromic battery, three charging methods may be chosen: 1) an external power source (for example, an electrochemical workstation), 2) oxygen in air, and 3) trace H_2O_2. We examined how different charging methods can affect the discharge capacity of the Al-tungsten oxide electrochromic battery. Figure 3 b shows the first discharge capacity and the specific accumulative discharge capacity of the recovered Al-tungsten oxide electrochromic battery recharged by oxygen and H_2O_2. The discharge capacity at −2 V for 60 s was 165 $mAh\,g^{-1}$. After spontaneous recovery in air for 24 hours, the battery recharged by oxygen was able to deliver a discharge capacity of 115 $mAh\,g^{-1}$ at −2 V, that is only 69 % of the first discharge. However, if H_2O_2 is applied to induce charging, the battery shows an extraordinarily high discharge capacity of 429 $mAh\,g^{-1}$ at −2 V, almost seven times larger than the best previously observed value for electrochromic batteries.[14] The discharge capacity of our

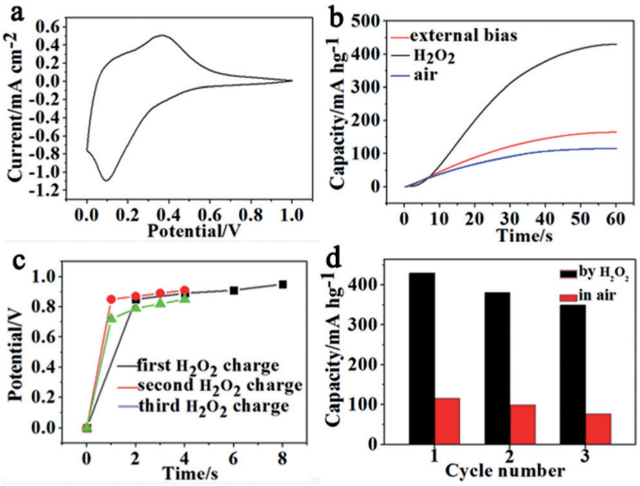

Figure 3. a) A typical cyclic voltammetry (CV) curve of the two-electrode Al-tungsten oxide battery is presented in $AlCl_3$ (1 M aqueous) between 0–1.2 V. b) The first discharge capacity and the specific accumulative discharge capacity of the recovered Al-tungsten oxide electrochromic battery recharged by oxygen and H_2O_2. c) The Al-tungsten oxide electrochromic battery is charged fleetingly by addition of trace H_2O_2 (three times in succession). d) Cyclic recharging of the Al-tungsten oxide battery by H_2O_2 or oxygen in air (three cycles).

electrochromic battery was greatly affected by the type of insertion ions. When an electrolyte based on Al^{3+} ions was used a high discharge capacity of more than 400 mAh g^{-1} was achieved, while the electrochromic battery performed at 120, 138, 142, 154, and 0.06 mAh g^{-1} without addition of H_2O_2, and 131, 154, 163, 217, and 0.09 mAh g^{-1} with addition of H_2O_2 for Li^+, K^+, Na^+, Mg^{2+}, and pure H_2O, respectively (Table 1; Supporting Information, Figure S6). Thus, in comparison with other conventional batteries, the best electrolyte for the Al-tungsten oxide electrochromic battery is an Al^{3+} ion-based electrolyte. The benefits of this electrolyte probably originate from the relatively small radius of Al^{3+} and the relative ease with which they may be inserted into the tungsten oxide host, as well as the high stability of the Al^{3+} intercalated phase.[7] We believe that the high capacity of the Al-tungsten oxide electrochromic batteries comes from, at least partially, a multivalent conversion in tungsten oxide (Supporting Information, Figure S7). It is well-known that tungsten ions can be reduced from the W^{6+} state to W^{5+}, W^{4+}, and even W^{3+}, according to Reaction (2). The theoretical discharge capacity of Al-tungsten oxide electrochromic batteries is based on the transfer of one, two, and three moles of electrons to W^{6+}, and was calculated to be 117.6 mAh g^{-1}, 235.2 mAh g^{-1}, and 352.8 mAh g^{-1}, respectively. Obviously, these values are much lower than our experimental value (429 mAh g^{-1}). Thus, other mechanisms must be responsible for the extremely high discharge capacity observed in the presence of H_2O_2. It is worth mentioning that tungsten oxide can be coordinated by $[O_2]^{2-}$ to form peroxotungstic acid ($H_2[W(O)_3(O_2)]$) in H_2O_2 solution, according to Reaction (4). During the discharge process, the formed peroxotungstic acid is reduced upon transfer of two of its electrons, becoming tungsten oxide (Reaction (5)). As a matter of fact, the presence of peroxotungstic acid is preliminarily supported by the Fourier Transform Infrared Spectroscopy (FTIR) spectra obtained from the samples before and after H_2O_2 treatment, where a broad and intense peak at 3447 cm^{-1} appeared in response to H_2O_2 addition, and could be assigned to the structural hydroxy group (Supporting Information, Figure S8). The switch from peroxotungstic acid to tungsten oxide could provide an additional discharge capacity of 235.2 mAh g^{-1}. Therefore, the real discharge process of Al-tungsten oxide electrochromic batteries in the presence of H_2O_2 is likely an intricate combination of the structure and valence state changes of tungsten oxide.

Table 1: A summary of discharge capacity of different aqueous electrolytes.

Ions	Without H_2O_2 [mAh g^{-1}]	With H_2O_2 [mAh g^{-1}]
Li^+	120	131
K^+	138	154
Na^+	142	163
Mg^{2+}	154	217
Al^{3+}	165	429
H_2O	0.06	0.09

The battery's incredibly fast charging time, brought about by the addition of H_2O_2, was confirmed by an electrochemical measurement of the open circuit potential. Figure 3c shows the change of open circuit potential of the recovered Al-tungsten oxide battery with increasing addition time, until it became saturated. It was found that the open circuit potential quickly increased to 1.2 V in just eight seconds, manifesting ultra-fast charging assisted by H_2O_2. Subsequently, the Al-tungsten oxide battery was subjected to cycling three times to evaluate its robustness. The recovered Al-tungsten oxide battery recharged by oxygen in air delivered a discharge capacity of only 77 mAh g^{-1} after three cycles, with a total capacity loss of 33% compared with the first discharge process (115 mAh g^{-1}; Figure 3d). In contrast, the capacity retention of the recovered Al-tungsten oxide battery recharged by H_2O_2 was 349 mAh g^{-1} after three cycles, which corresponds to a relatively small capacity loss of 18%, representing a better cycling performance.

In summary, we have successfully demonstrated an ultra-fast-charging, high-capacity Al-tungsten oxide electrochromic battery, in which the level of energy stored can be constantly and visually conveyed through recognizing variations in color. Our fabricated electrochromic battery presented a surprisingly high discharge capacity of 429 mAh g^{-1}, almost seven times larger than the best previously observed value for electrochromic batteries. The high capacity possibly comes from an intricate combination of structure and valence state changes of tungsten oxide. Additionally, the battery has the unique ability to charge in just eight seconds, 1000 times faster than other conventional batteries.

Experimental Section

Synthesis of $W_{18}O_{49}$ nanowires: The $W_{18}O_{49}$ nanowires were grown on an FTO-coated glass substrate with dimensions of 50 × 50 mm^2 using a previously reported approach. WCl_6 (0.099 g) was dissolved in absolute ethanol (30 mL) and FTO glass then placed in the as-prepared solution vertically, followed by a hydrothermal reaction at 180 °C for 12 h, and subsequent annealing at 200 °C in argon atmosphere to achieve close contact at the interface.

Preparation of the tungsten oxide electrochromic battery: The electrochromic battery device was fabricated by assembling the FTO glass coated with a film of $W_{18}O_{49}$ nanowires. A small Al sheet was attached onto one side of the conductive surface of another piece of FTO glass and both FTO glass slides packaged with epoxy. The electrolyte (1 M $AlCl_3$ aqueous solution) was dropped into the spacing between the two electrodes (film of $W_{18}O_{49}$ nanowires and the Al sheet).

Characterization: The transmittance spectra of the battery were monitored with a UV/Vis spectrophotometer (V660, JASCO). Electrochemical measurements were carried out with a CHI 660 electrochemical workstation in either a two- or three-electrode system at room temperature using $AlCl_3$ (1 M aqueous solution) as electrolyte. For the two-electrode configuration, the film of $W_{18}O_{49}$ nanowires on FTO glass was used as the working electrode and Al foil served as the counter electrode and the reference electrode. For the three-electrode system, Al foil and a Ag/AgCl electrode were used as the counter electrode and the reference electrode, respectively.

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