

# The potential valleys of silver oxide electrodes during pulse discharge

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## Abstract

The potential transient during pulse discharge is studied for ultra-thin silver oxide electrodes with special attention to the potential valleys. The potential valley appears in different ways depending on the history of charge and discharge undergone by the electrode and is attributed to highly resistive  $\text{Ag}_2\text{O}$  layers. The latter may exist on the surface of silver substrate (current collector) or inside the particles of active material. Moreover, the resistive  $\text{Ag}_2\text{O}$  layer may be partially reduced during current pulses and partially restored during pulse intervals, leading to complicated potential responses to the pulse discharge. To prevent the annoying potential valley, the silver electrode is suggested to be charged to an extent below the full conversion of Ag to  $\text{Ag}_2\text{O}$ . © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Zinc–silver battery; Silver electrode; Silver oxides; Pulse discharge

## 1. Introduction

Because of the superiority in power density, the zinc–silver system is still the top choice for applications where volume and weight are critical, such as high power pulse batteries which are supposed to be able to discharge at an unusually high current density in a pulse version. In conventional discharge, a fully charged zinc–silver oxide battery often shows two well defined voltage plateaus with a voltage valley appearing between the two plateaus; while during charge process, a voltage spike often appears instead [1]. In some reports, a less prominent voltage valley may be seen at the beginning of the discharge curve [2] but has little been discussed. In most conventional applications, the voltage valley is tolerable because it is not very deep (usually less than 0.1 V) and only appears in a short duration (seconds) in the course of a continuous discharge (typically hours). However, the situation for high power pulse batteries is much more severe. In pulse discharges, the duration of voltage valley may come to be comparable with that of a pulse and the valley may be several 10ths volts deep as we found in this work. Furthermore, we have also found that the voltage valley would appear in every successive pulses in a train of pulses. Obviously, it is an imperative task to solve the voltage valley problem for high power pulse batteries and the understanding of the cause of the voltage valley is apparently of significance to zinc–silver batteries in general.

About the voltage valley and spike between the two voltage plateaus, there have been numerous discussions in literature but views are still divided. Most researchers attribute the voltage valley in discharge and the voltage spike in charge to the high resistance of  $\text{Ag}_2\text{O}$  [3–5]. It seems reasonable in view of two aspects. On one side,  $\text{Ag}_2\text{O}$  is indeed highly resistive. On the other side, in the transition region between the high and low plateaus, the electrochemical interface must mainly consist of  $\text{Ag}_2\text{O}$ . Some authors suggested that the highly resistive  $\text{Ag}_2\text{O}$  would force electrical current to concentrate on some small areas not covered by  $\text{Ag}_2\text{O}$  and the sharply increased local current density may cause passivation during charge [4]. Besides the high resistivity of  $\text{Ag}_2\text{O}$ , adsorbed oxygen was claimed by a few researchers to be responsible for the spike in charge process [1,6]. Moreover, nucleation overpotential of the positive electrode was also thought to be a reason for the sudden voltage change in the transition region [7,8]. It seems that the problem of potential valley (or spike) of silver electrode is rather complicated and warrants further studies.

In the present paper, we report our recent works on the transient potential response of ultra-thin silver oxide electrodes in pulse discharge with special attention to the potential valleys.

## 2. Experimental

The silver electrode used in this work was the ultra-thin porous electrode which we developed specially for high power pulse batteries. The details of preparation and char-

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acterization of the electrode are to be reported elsewhere [9]. In brief, the electrode was prepared by oxidation and reduction of a silver foil 50  $\mu\text{m}$  thick in 0.1 mol/l HCl solution followed by charge–discharge cycling in 7 mol/l KOH for activation. The finished electrode had a thickness of 80  $\mu\text{m}$  which included a porous active material (about 22  $\mu\text{m}$ ) on each side and a solid silver layer in the center to serve as the electrical collector. The average diameter of the particles of active material was estimated to be 0.1  $\mu\text{m}$  from electrochemical measurements and SEM (scanning electron microscope) observation.

The silver electrode was charged in different versions and tested for pulse discharge performance. In most cases, the electrode was charged with constant current (60 mA/cm<sup>2</sup>) to a required charge. For the fully charged Ag<sub>2</sub>O electrode, the constant current charge was followed by constant potential charge at 0.7 V (versus zinc in the same solution). Caution was taken to ensure a uniform current distribution over the whole electrode surface [9]. The electrode potential was measured against a zinc electrode in the same solution via a Luggin capillary. Pulse discharge was performed on a homemade computer-controlled galvanostat with a data acquisition period of 30  $\mu\text{s}$ . The current pulses had an amplitude 0.4 A/cm<sup>2</sup> and lasted for 0.1 s with an interval 0.1 s between two neighboring pulses. The electrode was discharged with 10 successive pulses (called a set of pulses in the text ahead) for a time and there was a 2-min break between two adjacent pulse sets. Discharge was conducted in 7 mol/l KOH at 25 °C.

To examine the effects of dry shelf, a charged electrode was withdrawn from alkaline solution, washed thoroughly

with distilled water and dried in air. To study the effects of the substrate, another kind of silver electrode was prepared by plating silver on a Pt plate substrate in a cyanide plating bath. The deposited silver was then subject to above described processes to be converted to porous active material.

### 3. Results and discussion

In this section, we will first describe experimental findings obtained in different circumstances and then discuss these results with a proposed model.

#### 3.1. Pulse discharge of a newly charged AgO electrode

The newly charged AgO electrode here refers to the electrode that had been charged to oxygen evolution (called the fully charged AgO electrode in the text later) and was subject to pulse discharge immediately after completion of charge. Fig. 1 shows typical potential responses of the newly charged AgO electrode to sets of pulses in the high plateau, transition regions and low plateau, respectively. In the high potential region (Fig. 1a), the potential response appeared normal, i.e. it decreased monotonously with time in a single pulse, decreasing quickly first and then leveling off. This kind of potential change is expected for a porous electrode in the simplest situation (the physical parameters being time-independent and uniform throughout the active layer) and the characteristic time of potential decay is thought to be determined by the capacitance and resistance of the porous electrode [10].

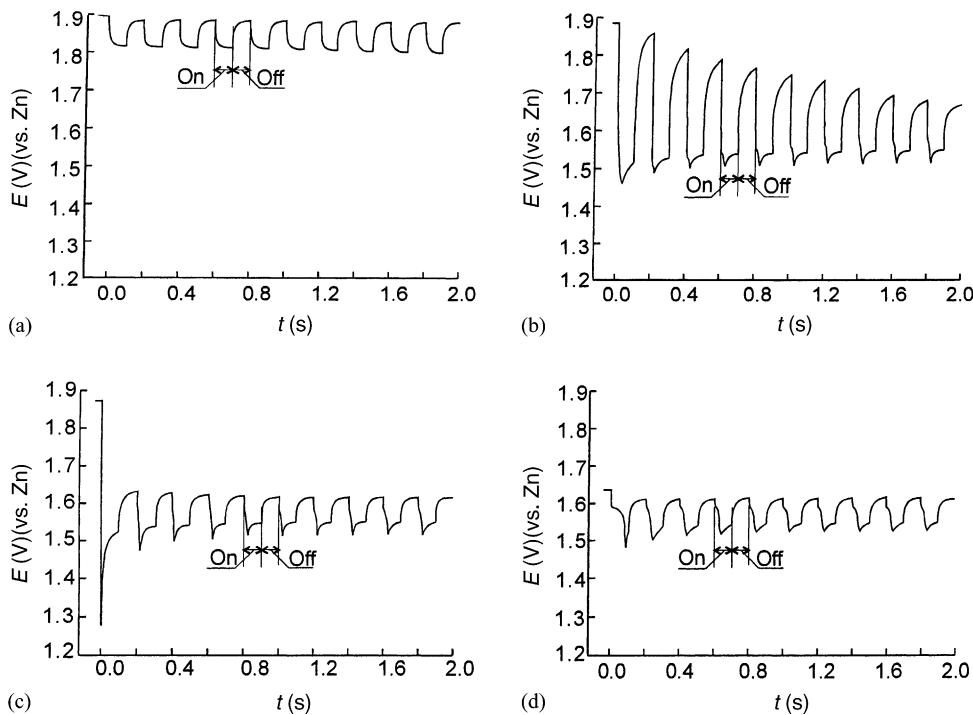


Fig. 1. Potential response of a newly charged AgO to pulse discharge: (a) high plateau region; (b) early stage in transition region; (c) the last set in transition region; (d) low plateau region. “On” and “off” refer to current pulse and interval, respectively.

In the transition region between the high and low plateaus, the potential response became complicated and no longer monotonous with time in a single pulse. A potential valley was seen in every pulse as shown in Fig. 1b and Fig. 1c with the valley bottom being well below 1.6 V. In Fig. 1b, the potential reachable at the end of an interval decreased with successive pulses, implying that the composition of the effective electrochemical interfaces had decreasing concentration of AgO and increasing concentrations of Ag<sub>2</sub>O and Ag. In a porous electrode with complicated composition and structures, all the electrochemical interfaces do not contribute equally to the current generated. The effective electrochemical interface here refers to the interfaces contributing the most to the electrode reaction (to generate current during discharge and to recover the potential during intervals) in comparison with the rest of electrochemical interfaces. It is also noted in Fig. 1b that the potential valleys become less deep with successive pulses and there is a twist visible on the down going course of potential for most pulses.

The potential profiles in the transition region had two common features. Firstly, during the 2 min of rest between neighboring sets of pulses the open circuit potential (OCP) could return to a value close to but slightly lower than the original value. Secondly, a potential valley occurred to every pulse in a set. However, there were some differences in different sets of pulses in the transition region. In the early stage of the transition region, the potential in pulse intervals could recover to values above the equilibrium potential of the low plateau (ca. 1.64 V) as shown in Fig. 1b. In contrast, in the last set of pulses in the transition region the potential in the intervals could never return to a value higher than the low plateau equilibrium potential. Moreover, the deepest valley always appeared in the last set of pulses in the transition region (Fig. 1c).

In the low plateau region, the OCP could never exceed the low plateau equilibrium potential and potential valleys occurred to all pulses (Fig. 1d), except for the first one or two pulses in a set in the late stage of discharge. Fig. 2 shows

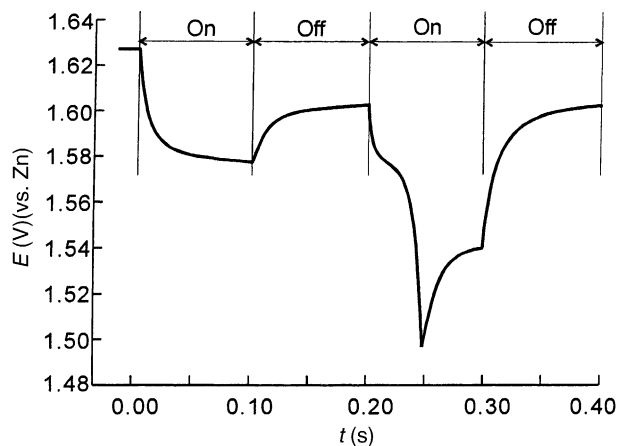


Fig. 2. The first two pulses in the 18th set of pulse discharge for a newly charged AgO electrode.

an enlarged view of the potential profile for the first two pulses in the 18th set of discharge. The potential change in the first pulse appeared normal (without potential valley!). However, the normal region was shortened and followed by a valley in the second pulse. In later sets of discharge, even the second pulse might show the normal response. By careful inspection into Fig. 1d, a short “normal” portion can be recognized prior to the valley in each of the pulses and the first pulse has the longest normal portion in the set shown. Looking back to Fig. 1b and Fig. 1c, the small twists there on the down going course of potential now can also be understood as manifestation of a short “normal” portion.

### 3.2. Pulse discharge of a fully charged AgO electrode after dry shelf

If a fully charged AgO electrode had been shelved in dry state for certain time (20 h in this work) before discharge, the potential response to pulse discharge in the high plateau region would be remarkably different from that described in the previous section. At the beginning of each pulse, the potential dropped from a value near 1.9 V down to 1.3 V, then the potential rose up and leveled off below 1.6 V (Fig. 3) to form a deep potential valley. In this region, the so-called high plateau was seen only in pulse intervals where potential approximately recovered to its open circuit value while the loaded potential was mainly in the low plateau potential region. There was a deep potential valley for each pulse though the situation improved slightly with increasing number of pulses. After three sets of discharge, the electrode entered into the transition region and then the low plateau region with potential transients similar to those described in Fig. 1b through Fig. 1d.

Fig. 4 is an enlarged view of potential change in a single pulse in the high plateau region for the shelved fully charged electrode. At the beginning and end of the pulse, there were interruptions in potential tracing. Since

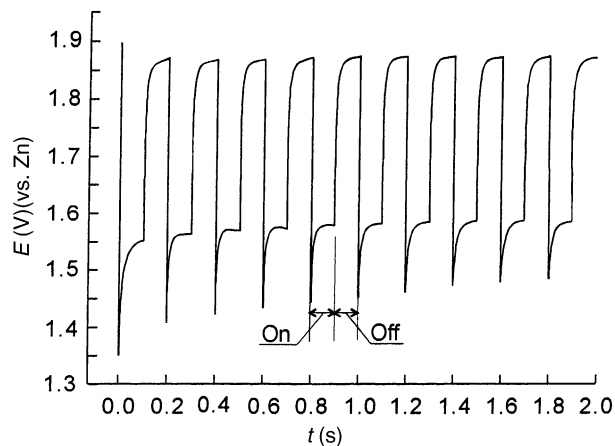


Fig. 3. Pulse discharge of a fully charged AgO electrode after 20 h of dry shelf.

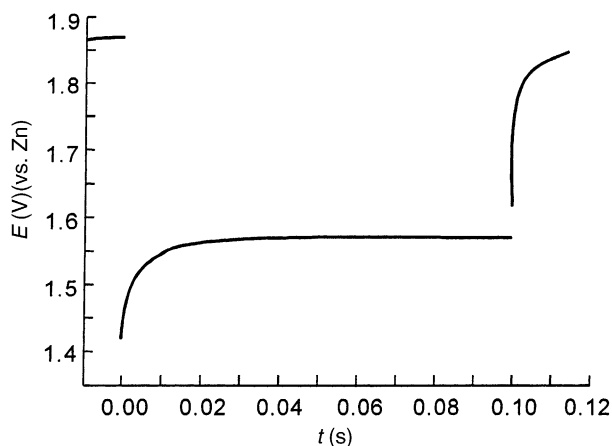


Fig. 4. Enlarged view of a single pulse in high plateau region for the fully charged AgO electrode after 20 h dry shelf.

the frequency of data acquisition was one data point per 30  $\mu\text{s}$ , the interruptions must imply rather fast potential changes accompanying the sudden current changes. Most probably, these potential interruptions were due mainly to ohmic drops. Fig. 4 indicates that the resistance was very large at the beginning of a pulse and much decreased at the end of the pulse.

In contrast to the description in the previous paragraph, the fully charged AgO electrode on Pt substrate behaved like the newly charged AgO electrode made from silver film. Regardless whether the electrode had experienced dry shelf or not, its pulse discharge performance remained the same, i.e. there was no potential valley in the high plateau region but valleys did appear in the transition and low plateau regions just like the situations depicted in Fig. 1.

From the above data, the potential valleys seen in pulse discharge may be divided into two basic categories. One occurs in the high plateau region for the shelved fully charged AgO electrode using Ag substrate as current collector. The occurrence of this type valley (denoted type I in the following text) needs three necessary conditions, i.e. using silver as the collector, being charged to high plateau potential and shelved for a sufficiently long time. Taking into account of the discussion on Fig. 4, it may be inferred that type I valley is brought about by a highly resistive layer formed on the surface of silver collector during shelf. Moreover, the resistive layer seems to be reduced to some extent in a pulse of discharge and partially recovered during the pulse interval. Another type valley (denoted type II) occurs in the low plateau region for all the electrodes mentioned above and had nothing to do with the collector. Therefore, type II valley must be caused by some changes in the active material instead of the changes on the collector surface. Like type I, the causes of type II valley seems to be depressed to some extent during discharge pulses and partially recovered in intervals.

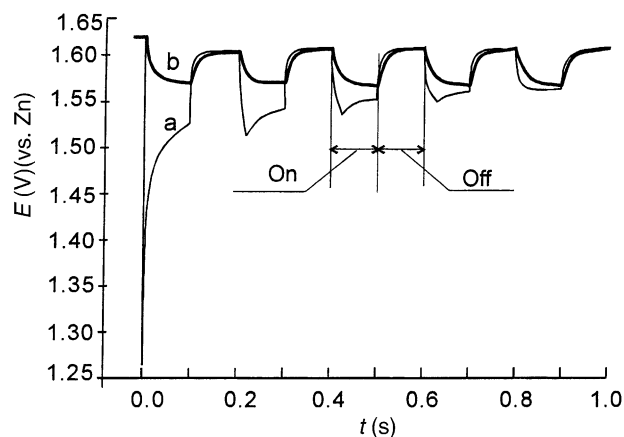


Fig. 5. Pulse discharge of Ag<sub>2</sub>O electrodes: (a) fully charged; (b) partially charged.

### 3.3. Pulse discharge of Ag<sub>2</sub>O electrodes

Two Ag<sub>2</sub>O electrodes were tested in this work and both were made from silver film in the way described above. One test electrode was charged galvanostatically first and then potentiostatically at 1.7 V (versus Zn) to ensure all the active material to be converted to Ag<sub>2</sub>O. This electrode is called the fully charged Ag<sub>2</sub>O electrode in the text below. In continuous discharge at 0.4 A/cm<sup>2</sup>, this electrode released 4.5 C/cm<sup>2</sup>. Another test electrode was charged galvanostatically to 2.5 C/cm<sup>2</sup> (about a half of the capacitance based on Ag<sub>2</sub>O) and is called the partially charged Ag<sub>2</sub>O electrode.

As shown in Fig. 5, the two electrodes responded to current pulses quite differently. The fully charged one exhibited a deep potential valley in the first pulse (Fig. 5a), however, the valley shrank quickly with time and the potential response became almost normal after four pulses. In contrary, the partially charged Ag<sub>2</sub>O electrode showed perfectly normal response without potential valley at all. This comparison may imply that the fully charged Ag<sub>2</sub>O electrode was highly resistive but became conductive quickly on discharge. A small amount of metallic silver produced in discharge seems to be able to make the electrode sufficiently conductive to show normal behavior in later discharge pulses.

Besides the absence of potential valley, the partially charged Ag<sub>2</sub>O electrode was also superior in terms polarization to the other electrodes mentioned above. It is worth noting that the shelved fully charged AgO electrode behaved much worse in this aspect than the partially charged Ag<sub>2</sub>O electrode though the former obviously had more electricity storage. The shelved AgO electrode not only showed deep potential valley in every pulse in the high plateau region but the leveling off potential within a single pulse was also lower than that of the partially charged Ag<sub>2</sub>O electrode, namely the former showed lower loading potential than the latter. Moreover, the partially charged Ag<sub>2</sub>O electrode showed

no appreciable change on dry shelf (data over months of shelf had been obtained at the time this paper was written). Therefore, from the view point of practical applications to pulse batteries, the partially charged  $\text{Ag}_2\text{O}$  should be the best choice.

### 3.4. Correlation between OCP and the valley potential

Fig. 6 shows the correlation between the OCP and the valley potential (VP) for the fully charged  $\text{AgO}$  electrodes with and without dry shelf. In pulse discharge, the electrode was discharged by a series of pulse sets with a 2-min break between two adjacent sets. The OCP was taken at the end of each 2-min break just before a new set of discharge pulses. The VPs were the potential at the bottom of the deepest valley in a single set of pulses. In most cases, the deepest valley occurred in the first pulse in a set of pulses. In the later sets of pulse discharge for a given electrode, however, the first a few pulses might have no valley and the deepest valley was always seen in the pulse immediately following the preceding valley-free pulses.

As shown in Fig. 6, there was no valley for the newly charged  $\text{AgO}$  electrode till the 5th second of accumulated net discharge time where the OCP began to decrease. The deepest valley occurred at the onset of sudden drop of OCP (the 7th second of accumulated discharge time). The period from the 5th to the 7th second corresponds to the transition region shown in Fig. 1b and Fig. 1c. In the low plateau region (OCP 1.63–1.64 V), VP was not much changed except for the a few sets at early stage where VP values were slightly higher (valley shallower).

For the shelved fully charged  $\text{AgO}$  electrode, the correlation between OCP and VP in the low plateau region and the transition region was almost a duplicate of that for the newly charged one. Unlike the newly charged one, however, in the high OCP region the shelved  $\text{AgO}$  electrode showed potential valleys starting from the first set of pulses and the VP

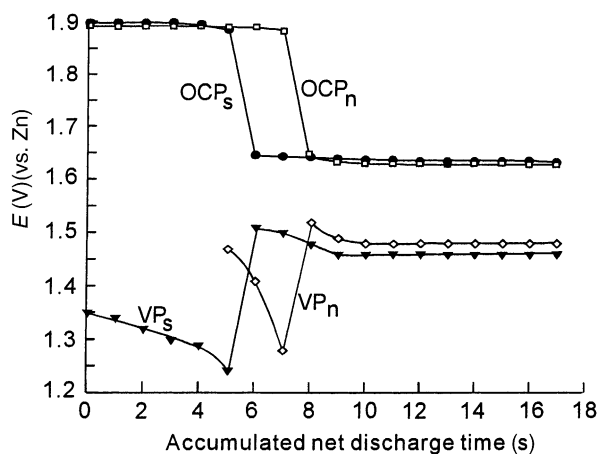


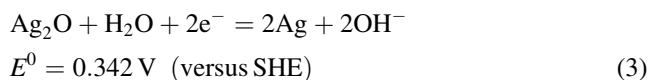
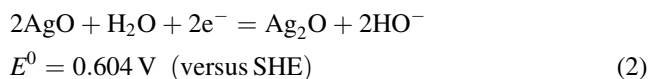
Fig. 6. Changes in OCP and VP with accumulated net discharge time for fully charged  $\text{AgO}$  electrodes. Subscripts n and s refer to the newly charged electrode and shelved electrode, respectively.

values went down with accumulated net discharge time till the minimum which appeared at the 5th second, 2 s earlier than the newly charged one.

### 3.5. The origins of potential valley

#### 3.5.1. The $\text{AgO-Ag}_2\text{O-Ag}$ system

The rich information gathered in the previous sections provides a sound experimental basis for understanding the cause of the potential valleys. In discussion of the origins of the potential valleys, the following three reactions [1,11,12] should be taken into account



Reaction 1 can be regarded as a combination of reactions 2 and 3. As seen from the standard potentials, reaction 1 will take place spontaneously when Ag and  $\text{AgO}$  are in coexistence. This reaction has been well recognized but researchers are divided on its rate constant [4,5,13]. Obviously, both electrochemical and chemical mechanisms are valid in electrolyte for reaction 1 while only solid state chemical reaction pathway is available in dry shelf. The location and density of the products from reaction 1 may be different for electrochemical and chemical mechanisms. Solid state chemical reaction can occur only in the places where Ag and  $\text{AgO}$  are in direct contact, resulting in  $\text{Ag}_2\text{O}$  concentrated in the interfacial areas. Thus chemically produced  $\text{Ag}_2\text{O}$  should tend to form a dense layer which is expected to be highly resistive. In contrast, the  $\text{Ag}_2\text{O}$  produced through electrochemical reactions may distribute in a relatively larger space in the metallic Ag matrix, not just confined to the interfaces between  $\text{AgO}$  and Ag and is less likely to form a highly resistive dense  $\text{Ag}_2\text{O}$  layer. In reality, however, distinguishing between the two mechanisms may not be a simple clear cut. The so-called dry state in this work should not be regarded as absolutely water-free. On the other hand, because of the solution resistance, the electrochemical production of  $\text{Ag}_2\text{O}$  would be favored in places close (though not confined) to the border areas between  $\text{AgO}$  and Ag.

#### 3.5.2. Type I valley

Following the above discussion, it is conceivable that a highly resistive dense  $\text{Ag}_2\text{O}$  layer would develop on the silver substrate (current collector) during shelf for a fully charged  $\text{AgO}$  electrode regardless whether the electrode is dry or immersed in a solution. This layer would cause a large ohmic drop on discharge. As shown in Fig. 3, the potential could be brought down to 1.35 V, much below the equilibrium potential for  $\text{Ag}_2\text{O/Ag}$  couple (ca. 1.64 V). At such

low potentials, the resistive  $\text{Ag}_2\text{O}$  would be reduced, resulting in a decrease of overpotential. Such potential drop and rise caused potential valleys of type I. The repetitive appearance of type I valleys implies that the resistive layer could be partially repaired by the reaction 1 during the interval that follows the pulse. Obviously, it is necessary for type I valley to occur to satisfy three conditions: (1) the substrate (electrical collector) is metallic silver; (2) there is sufficient amount of  $\text{AgO}$  in the active material to oxidize the substrate surface; (3) sufficient shelf time for accumulation of resistive  $\text{Ag}_2\text{O}$ . This analysis is in agreement with the observations mentioned in Section 3.2. This can explain why the  $\text{AgO}$  electrodes on Pt substrate and the newly charged  $\text{AgO}$  electrodes on silver substrate did not show type I valley; the former did not meet the first condition while the latter lacked the third condition.

By the same reasoning, type I valley should also occur at the beginning in conventional (continuous) discharge for a shelved  $\text{AgO}$  electrode. We did see this expected phenomenon with our ultra-thin silver oxide electrode. Type I valley has been scarcely seen in the literature perhaps because it is too short to be noticed in conventional discharge with time scales of hours. However, recognizable type I valley was indeed found in literature though ignored previously [2].

According to the above discussion, it should also be expected that a voltage spike would take place at the beginning of charging processes for a shelved partially charged  $\text{AgO}$  electrode. This deduction is supported by a few reports in literature. For example, a voltage spike was found at the beginning of charging for an incompletely charged zinc–silver oxide battery and also found at the beginning of each period of square wave charging process (the latter case could be regarded as charging with long period pulses). [14,15].

### 3.5.3. Type II valley

It may be appropriate at this point to recall the mainly experimental findings relevant to type II valley. One important feature of type II valley was a segment of normal potential response prior to the occurrence of the valley in a single pulse (Fig. 1d). The normal segment might be long enough to span one or even two pulses (Fig. 2) but in most pulses it only manifested as a twist near 1.6 V in the potential down going course at the beginning of a pulse. Another important feature of type II valley is that it occurred in the low potential region but only occurred with those electrodes which had undergone discharge in the high potential region. Besides, type II valley occurred regardless the material of the substrate (collector). Therefore, the cause of the type II valley must be in the active material itself.

In order to understand type II valley, the coexistence of  $\text{AgO}$ ,  $\text{Ag}_2\text{O}$  and  $\text{Ag}$  in the active material must be taken into account. The low plateau region is usually considered to be governed by  $\text{Ag}_2\text{O}/\text{Ag}$  couple. However, it has been reported that  $\text{AgO}$  does exist in the active material in the low OCP

region for a silver oxide electrode which has experienced discharge in the high OCP region [16]. In this case, the low plateau OCP (slightly above 1.6 V versus Zn) is actually a mixed potential of reactions 2 and 3 but largely shifted to the value determined by reaction 3, obviously because reaction 3 is overwhelming in exchange current over reaction 2. It is not new that a system consisting of  $\text{AgO}$ ,  $\text{Ag}_2\text{O}$  and  $\text{Ag}$  simultaneously could show a potential around 1.6 V. In fact, partial chemical reduction of  $\text{AgO}$  to  $\text{Ag}$  was reported for manufacturing zinc–silver oxide batteries which contained  $\text{AgO}$  but discharged only at low plateau potential [17]. In these cases, the outer part of a particle of the active material is mainly composed of metallic  $\text{Ag}$  and  $\text{Ag}_2\text{O}$  while  $\text{AgO}$  remains in the core.

According to reaction 1, the coexistence of  $\text{AgO}$  with metallic silver must result in formation of  $\text{Ag}_2\text{O}$ . The potential profiles in Fig. 2 indicate that there are two different kinds of  $\text{Ag}_2\text{O}$ . The first pulse showing perfectly normal potential profile and the small normal segment in the second pulse in Fig. 2 suggests the presence of a kind of  $\text{Ag}_2\text{O}$  which showed normal discharge behavior. To distinguish from another kind of  $\text{Ag}_2\text{O}$ , we call it the advantageous  $\text{Ag}_2\text{O}$ . This advantageous  $\text{Ag}_2\text{O}$  is thought to be produced mainly through electrochemical mechanism of reaction 1 (i.e. conjugated reactions 2 and 3) and it is similar in nature to the  $\text{Ag}_2\text{O}$  in the partially charged  $\text{Ag}_2\text{O}$  electrode described in Section 3.3. The advantageous  $\text{Ag}_2\text{O}$  should be in a dispersed form in the conducting network of metallic silver so that the high resistivity of  $\text{Ag}_2\text{O}$  itself does not affect discharge deleteriously. Obviously, a large surface area of metallic silver is favorable for the formation of the advantageous  $\text{Ag}_2\text{O}$ . This may explain why the normal potential transient spanning a whole pulse shown in Fig. 2 could be seen only when the accumulated discharge time was sufficiently long (a large metallic silver surface became available).

The second kind of  $\text{Ag}_2\text{O}$  is thought to be relatively dense and concentrated on the border areas between  $\text{AgO}$  and  $\text{Ag}$  in the particles of active material. Because of its high resistance and thereby being difficult to discharge, we call it the disadvantageous  $\text{Ag}_2\text{O}$ . In discharge, the advantageous  $\text{Ag}_2\text{O}$  came to effect first and when it exhausted the disadvantageous one took over, resulting in a more or less normal potential response followed by a sharp potential drop. The reduction of the disadvantageous  $\text{Ag}_2\text{O}$  to metallic silver caused a decrease of resistance and the potential rose gradually to form a potential valley.

Both kinds of  $\text{Ag}_2\text{O}$  can be produced by reaction 1 in pulse intervals (0.1 s) and during the rest time between pulse sets (2 min), resulting in repetitive appearance of type II valleys in successive pulses. Obviously, the amount of both kinds of  $\text{Ag}_2\text{O}$  produced in the rest time between pulse sets (2 min) should be much more than those produced in the interval (0.1 s) between pulses in a single set. Therefore, the longest normal segment in a set of pulses must appear in the first pulse and the deepest valley in a set of pulses must

be the first valley in the set (not necessarily in the first pulse). These deductions are in agreement with experimental observations (Fig. 1d and Fig. 2, for example).

The potential valley shown in Fig. 5a provides an additional support to the above proposed theory for the valleys. The fully charged  $\text{Ag}_2\text{O}$  electrode obviously consisted entirely of  $\text{Ag}_2\text{O}$  in its active material and the surface layer of substrate. This dense  $\text{Ag}_2\text{O}$  should be highly resistive and understandably could cause a very deep valley for the first discharge pulse. Unlike the situation of Fig. 1, in the fully charged  $\text{Ag}_2\text{O}$  electrode there was no  $\text{AgO}$  which is necessary for the regeneration of  $\text{Ag}_2\text{O}$  through reaction 1. Therefore, the valley vanished quickly in a just few successive pulses as  $\text{Ag}_2\text{O}$  reduced (Fig. 5a).

### 3.5.4. The transition region

The experimental findings of the transition region can also be explained in the framework of the above proposed theory. Because the main features of the transition region were independent of both the substrate and shelf time, they should be related to the changes occurring in the active material. Therefore, the potential valleys in the transition region (Fig. 1b and Fig. 1c) should essentially be type II valleys. In fact, the lower part for the most pulses in Fig. 1b look very similar to Fig. 1d (typical type II valleys). The main difference is that the potential in intervals could exceed the  $\text{AgO}/\text{Ag}_2\text{O}$  equilibrium potential in Fig. 1b but not in Fig. 1d. This can be explained by the presence of more  $\text{AgO}$  in the transition region than in the low plateau region. However, the storage of  $\text{AgO}$  decreased with progressive discharge and the reachable potential in intervals decreased as shown in Fig. 1b. In the last set of the transition region (Fig. 1c), the OCP before discharge was above 1.85 V but the potential could never recover to a value above the  $\text{AgO}/\text{Ag}_2\text{O}$  equilibrium (ca. 1.64 V) during discharge because of lack of sufficient  $\text{AgO}$  storage.

Based on the above discussions, it is easy to understand why the partially charged  $\text{Ag}_2\text{O}$  electrode showed the best pulse discharge performance. This electrode contained only  $\text{Ag}_2\text{O}$  and  $\text{Ag}$  and, moreover, all the  $\text{Ag}_2\text{O}$  was in the advantageous form. The large amount of advantageous  $\text{Ag}_2\text{O}$  in coexistence with  $\text{Ag}$  provided a high apparent exchange current. Therefore, the overpotential of this electrode was the smallest among the electrodes studied in this work. Because there was no  $\text{AgO}$ , it was impossible to produce the disadvantageous  $\text{Ag}_2\text{O}$  and, therefore, potential valley could never occur.

In all the above discussions on potential valleys, the nucleation overpotential suggested by some workers is not invoked [7,8]. This does not mean that the nucleation overpotential does not exist at all. However, the experimental results in this work do not provide any supports to the nucleation theory for the valleys. For example, the repetitive appearance of potential valley in successive pulses is not

in favor of, though not absolutely against, the nucleation theory.

## 4. Summary

The pulse discharge of silver oxide electrodes often sees potential valleys which appear in successive pulses. The observed valleys may be classified into two categories (types I and II) and both are thought to be caused by the high resistance of the  $\text{Ag}_2\text{O}$  due to the reaction between  $\text{AgO}$  and  $\text{Ag}$ . Type I valley occurs in the high OCP region and the highly resistive  $\text{Ag}_2\text{O}$  layer on the surface of silver substrate (collector) is considered to be responsible for the valley. Type II valley mainly appears in the low OCP region for electrodes which have undergone discharge in the high plateau region. Type II valley is thought to be caused by the resistive  $\text{Ag}_2\text{O}$  in the interface region between  $\text{AgO}$  and  $\text{Ag}$  inside the particles of active material. The key to eliminating potential valley is to avoid the coexistence of  $\text{AgO}$  with metallic  $\text{Ag}$ . A non-silver substrate, if any, may prevent type I valley but not type II. A simple and effective measure to get rid of the annoying valley is charging the electrode with an amount of charge less than that needed for full conversion of the active material to  $\text{Ag}_2\text{O}$ . The pulse discharge of this partially charged  $\text{Ag}_2\text{O}$  electrode is not only free of potential valley but also low in polarization.

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