Capacitors Consisting of an Aqueous Electrolyte of the Widest Potential Window—Development towards the Recovery of Regenerating Energy of Automobiles—

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Abstract

An aqueous capacitor has been developed mainly for the purpose of recovering the regenerating energy for automobiles. A rapid charging within few seconds is required as well as the safety and the considerably large energy density. We have made two types of capacitors using a saturated sodium perchlorate aqueous solution (SSPAS) as an electrolyte, i.e., one consisted of a mixture of graphite and activated carbon, and the other mixtures of graphite and metal oxides. The former was an electric double layer type its energy density being 23 Wh/kg under the 70% of activated carbon and the applied voltage of 2.5 V. The generation of gases was not detected until the cut-off voltage 2.7 V using a SS444 foil as a current collector. Experiments using a titanium foil as a current collector revealed that the charge and discharge capacities were independent of temperatures from 0 to 60°C. In the applied electric current density of 20 mA/cm², the capacity was determined to be 0.03 mAh/cm² with the coulombic efficiency of 100% leading to the charging time of 5.4 s. The present result confirms a feasibility of recovering the regenerating energy for automobiles.

Keywords: Aqueous Electrolyte, Sodium Perchlorate, Potential Window, Capacitor

1. Introduction

It is no doubt that aqueous electrolytes are superior with respect to the fundamental electrochemical nature such as an electrical conductivity as well as the safety of non-combustibility to any organic electrolytes. Particularly, the safety is the first priority for automobiles. However, aqueous electrolytes have a serious weak point that their potential windows are narrow. As a matter of fact, the theoretical potential window of water is known to be 1.23 V. This leads to a restriction for the applied voltage resulting in the energetic disadvantage, and hence aqueous electrolytes have not been used practically for capacitors. In an earlier paper, we reported that a saturated sodium perchlorate aqueous solution (SSPAS) showed the extreme inertness for the electrochemical decomposition, giving a potential window of 3.2 V, which is largest of any aqueous solutions.

These results would enable us to overcome the weak point of aqueous electrolytes. Besides our study to widen the potential window of aqueous electrolytes, there have been other reports. Okada et al. reported the study on a sodium-ion battery using 17 m (mol/kg water) NaClO₄ aqueous solution, the condition of which is similar to SSPAS. The concentration of sodium perchlorate obtained from the study are 0.03 mAh/cm² with the coulombic efficiency of 0.64. However, the specific energy density of the capacitor is quite small.

In the earlier paper, we explained the reason of widening the potential window as follows. Sodium perchlorate is extremely soluble in water, its solubility being 209.6 g in 100 ml water at 25°C, that is, 17.1 mol in 1 L water. Under such a highly concentrated condition, less than four water molecules exist per one sodium ion, which is smaller than the first coordination sphere of Na⁺. Furthermore, ClO₄⁻ also restricts the movement of water. Since water molecule is highly restricted by Na⁺ and ClO₄⁻, hydrogen bond could be weakened or destroyed. This might strengthen the O–H bond of H₂O in SSPAS due to the increased electron density between O and H. The ¹H NMR measurement of water supported the above fact, because the chemical shift towards the higher magnetic field in SSPAS was coincide with an increase in the electron density around H. The ¹H NMR signal of water in SSPAS indicated the restriction of ¹H relaxation due to the lack of neighboring ¹H.

In the case of NaClO₄, the molality of saturated NaClO₄ is 17.1 m (m = mole per 1 kg of solvent water) at 25°C. The concentration of saturated solution is highly dependent on temperature like as 16.4 m at 20°C and 18.1 m at 30°C. Recently, a number of papers were concerned for the development of capacitor using aqueous electrolytes. Kondo and Yuasa et al. used SSPAS as an electrolyte for the capacitor containing boron-doped diamond powders to determine the energy density of approximately 20 Wh/kg. In a paper by Chinese Academy of Science, various aqueous electrolytes were compared with organic ones based on the costs as well as the electro-chemical performances of these electrolytes.

The present paper is aimed for further development of aqueous capacitors using SSPAS. Our final goal is to establish an aqueous...
capacitor towards the recovery of regenerating energy for automobiles.

1.1 Comparison of SSPAS with other electrolytes

The study by X. Bu, X. Yan et al.5 of Chinese Academy of Science is of specific worth, because they compared various electrolytes based on a variety of viewpoints such as the costs and the electrochemical behavior. Major electrolytes treated are as follows: 17 m NaClO₄ aqueous solution, 21 m LiTFSI/H₂O (LiTFSI Lithium bis(trifluoro-methanesulfonylimide), 1.6 m Et₄NBF₄/ACN (Et₄NBF₄ tetraethyl-ammonium tetra-fluoroborate and ACN acetonitrile) and 1.0 m Et₄NBF₄/PC (PC propylene carbonate). With respect to the costs of these electrolytes, 17 m NaClO₄ aqueous solution is nearly 1/10 compared with other electrolytes. In the charge-discharge curves, the large electric current of 20 A/g is most important, because a large current should be required for the recovery of regenerating energy. In the charge-discharge curves, only 17 m NaClO₄ aqueous solution keeps a typical symmetric triangle shape with a high coulombic efficiency in spite of the high electric current density. X. Yan et al.5 concluded that the super concentrated sodium perchlorate aqueous solution exhibits comparable energy density, a high power density and a much lower price compared to commercial non-aqueous electrolytes.

2. Experiment

2.1 Coin type cell

The production of a coin type capacitor was described in the earlier paper.1 Galvanostatic and CV measurements were carried out by using an instrument of Bio-Logic VSP and also an Electrofield Co., Ltd. ABE1028.

2.2 Capacitor consisting of laminated layers

A laminate capacitor is of far advantage over a coin type capacitor in regard to the connection between a current collector and an active material, and to the production of large scale capacitors. In order to reduce the inner resistance, each cell should be made as thin as possible. As a current collector a SS444 (20 µm ferrite stainless steel) foil was used. An active material, a mixture of graphite and activated carbon (a graphite mixture), was coated over the surface of the current collector, and then permeated with the electrolyte (SSPAS) as shown in Fig. 1. The lamination of cells to multiple layers was also made.

3. Results and Discussion

3.1 Aqueous electrolytes

It has been known that the electrical conductivity of sodium perchlorate aqueous solution increases with increasing its concentration and reaches the maximum at the concentration between 3 and 5 M to be around 140 mS/cm at 25°C.16 Therefore, saturated sodium perchlorate aqueous solution (SSPAS) is disadvantageous with respect to the electrical conductivity compared with dilute aqueous solutions. We measured the electrical conductivity of SSPAS at various temperatures. As illustrated in Fig. 2, the electrical conductivity was found to change very sensitively with temperature, e.g., 62.0 mS/cm at 0°C, while 159 mS/cm at 59.8°C. Later on, such a difference in the electrical conductivity will be taken into account in charge-discharge cycles. There is an advantage in SSPAS, however, to lower its freezing point as low as −40°C17 and to elevate the boiling point higher than 110°C.

3.2 Potential windows in saturated aqueous solutions of various alkali and alkaline earth perchlorate salts

CV measurements were carried out for saturated aqueous solutions of various perchlorate salts. A glassy carbon for a working electrode, a platinum for a counter electrode and a Ag/AgCl as a reference electrode were used. All measurements were made by a scan rate of 1 mV/s and at 25°C.
weaken the hydrogen bond. The same reason is expected in other solutions. However, it is a little different in Li⁺. Since Li⁺ is weakly shielded by only two orbit electrons, and hence, water is strongly coordinated to Li⁺ allowing to have a second hydration sphere unlike other alkali ions.¹⁸,¹⁹ Therefore, despite relatively poor solubility of LiClO₄ in water, that is 59.8 g in 100 g water, water could be restricted to be free. In the case of saturated Mg(ClO₄)₂ aqueous solution, the CV behaves different from others. This might owe to the non-equilibrium hydrolysis of Mg²⁺ forming an insoluble MgO prior to the reduction.

3.3 Graphite-based capacitor

Coin type capacitors consisting of graphite only, and the mixture of graphite and activated carbon were made using SSPAS as the electrolyte. In the earlier paper,¹ galvanostatic charge-discharge curves were measured as shown in Fig. 4, where only graphite was contained in (a), while in (b) the mixture of graphite and activated carbon. The charge-discharge curve (a) revealed a typical shape of an electric double layer capacitor, while that of (b) distorted from a typical shape. The distortion may be attributed to the electrical loss, which might be caused by the thick coin type electrodes. As described later, charge-discharge curves were linear in laminate cells. The addition of activated carbon to the graphite mixture raises the energy density, i.e., the energy density for graphite only was 0.45 Wh/kg, while 18.7 Wh/kg in the presence of 40% of activated carbon. In Fig. 4(a), measurements were repeated 10,000 times at the cut-off voltage of 3.2 V and the stability of curves reflect the wide potential window of SSPAS.

3.4 Capacitors consisting of mixtures of graphite and metal oxides

It was found in the earlier paper¹ that the addition of metal oxides, such as Fe₂O₃, Fe₃O₄, V₂O₅ and RuO₂ to graphite-based negative electrodes brought remarkable gains in the energy density and the shapes of galvanostatic charge-discharge curves differ from those of electric double layer capacitor. Typical galvanostatic charge-discharge cycles of coin type capacitors are shown in Fig. 5(a) for a symmetric capacitor containing Fe₂O₃ in both negative and positive electrodes, and in Fig. 5(b) for an unsymmetrical capacitor containing Fe₂O₃ only in the negative electrode.
The addition of MnO₂ to the positive electrode increases the energy density and the combination with Fe₃O₄ in the negative electrode gave a large energy density of 36.2 Wh/kg.¹

3.5 Charge and discharge mechanism of capacitors containing metal oxides

The role of RuO₂ in capacitors has been studied most extensively. The following mechanism is generally believed: ²⁰

\[
RuO₂ + xH^+ + xe^- \rightarrow RuO_{2-x}(OH)_x
\]  
where, \(0 \leq x \leq 2\)

If \(x\) is larger than 1, the oxidation state of Ru changes and this indicates that a redox reaction takes place during charge-discharge cycles. However, these earlier studies were made in dilute aqueous solutions and hence the maximum applied voltage was restricted below 1 V. Such dilute solutions are incommensurable with SSPAS as electrolytes. Therefore, we have explored to develop a mechanism explaining the role of the metal oxides under the high applied voltage. The oxidation states of metals are the key to explain the mechanism. For this purpose, XRD and XPS measurements were carried out.¹ The oxidation state of metals in both negative and positive electrodes was not changed during charge-discharge cycles. At the same time, the graphite kept same in structural and electronic configurations. Although further experiments are in progress, we propose a synchronous electron absorption and release mechanism based on the present results as described by the following Eqs. (2) and (3).

In the negative electrode, an electron is absorbed into the inside of structures in metal oxides, where the oxidation states of metals remain unchanged.

\[
MO_x + ne^- \rightarrow MOx^{n^-}
\]  
(2)

The defect in structures of metal oxides is known in transition metal oxides to make positive or negative holes.²¹ In such defect structures, an electron could be absorbed in the structures. On the other hand, in the positive electrode, an electron is released from graphite in order to keep electric neutralization as expressed by Eq. (3). Metal oxides in the positive electrode could behave similarly as graphite.

\[
C \rightarrow C^{n+} + ne^- 
\]  
(3)

The graphite-based capacitors containing metal oxides is promising for large energy densities being close to the region of secondary batteries and the synchronous electron absorption and release mechanism explains the experimental results. However, there has not been yet a conclusive evidence for the above mechanism and further experiments should be necessary.

3.6 Gas generation from cells during charge-discharge cycles

It is absolutely necessary to observe whether gas is generated or not during charge-discharge cycles under such an unknown territory of the high applied voltage in aqueous solutions. For this purpose, we made a pressure vessel, in which a laminate cell was confined, and measured the pressure in the inside of vessel by an instrument of Nihon Pisco Co., Ltd. SEU11, its resolution being 250 Pa, in order to observe the released gasses from the cell. Experiments were performed under various cut-off voltages from 2.0 to 3.0 V with a weak applied electric current density of 1 mA/cm². A SS444 was used as a current collector. Five minutes interval was set between the discharge and charge to use up electricity. The charge-discharge curves are shown in Fig. 6, where the inside pressure is represented by red curves. The charge-discharge curves are found to be stable at the cut-off voltage from 2.0 to 2.7 V (Fig. 6(a)) and the inside pressure was kept constant under these conditions. However, at the cut-off voltage 3.0 V, it took time to attain to the maximum applied voltage at the beginning of the first cycle and at the same time the inner pressure increased remarkably indicating the gas generation (Fig. 6(b)). After the second cycle, the charge-discharge curves became stable keeping the inner pressure constant. We presumed that the gas generation would be attributed to a partial corrosion of the current collector (SS444 foil) at the beginning of the first cycle at the cut-off voltage 3.0 V. However, other possibilities cannot be ruled out at the moment. The charge and discharge cycles were repeated for 80 hours at the cut-off voltage of 2.5 V in order to observe the stability of the cell for long cycles (Fig. 7). The inner pressure was kept constant for 80 hours indicating that the cell was stable without generating gas during the operation time.

3.7 IR drop

An IR drop in capacitor is generally believed to indicate an internal resistance. However, this is not always true, because other origin is possibly involved in the IR drop, e.g., an interfacial resistance between a current collector and a cathode/anode layer or a thickness of electrode layer. If a resistance arises between a current collector and an active material at the time in turning on switch, the resistance would be involved in the IR drop and also in the start of charging. As demonstrated in Fig. 4 and Fig. 5 in coin type cells, the changes in cell voltage at the time 0 are closely the same in charge and in discharge. In such a case, the IR drop could be affected by the switch-on resistance due to a poor contact between a

![Graph showing charge-discharge curves](image-url)
current collector and an active material. Later on in Fig. 13, the IR drop was not observed in a laminate cell using a titanium foil as a current collector. The remarkable difference in the values of IR drop observed in coin type and laminate cells, i.e., 0.5 V and nearly 0 V, respectively, indicates that the IR drop in the present coin type cells is controlled by the contact resistance rather than the inner resistance. Although we do not have an evidence, the thickness of active material appears to contribute to the IR drop owing to the diffusion of ions, which would be accompanied by a resistance.

3.8 Single laminate cell and an assembly of laminated multiple cells

We made a single laminate cell and also an assembly of laminating ten cells each cell being connected in parallel using a sodium perchlorate aqueous solution saturated at 23°C as the electrolyte. The latter we call hereafter as simply a ten laminate cell. Charge and discharge measurements were carried out for both the single and ten laminate cells under the same condition, where 1 mA/cm² of electric current was applied for the single cell, and ten times more electric current for the ten laminate cell, where approximately 1 mA/cm² of electric current is expected to apply for each cell on average. Therefore, charge-discharge curves in the ten laminate cell show the average of ten laminated cells. The capacity for the charge and discharge, and the coulombic efficiency measured at various cut-off voltage from 2.0 to 2.5 V are plotted against the cycle numbers from 0 to 120 are shown in Fig. 8(a) for the single cell and for the ten laminate cell in Fig. 8(b). Measurements were made at 25°C.

In Fig. 8, the similarity in the single and ten laminate cells indicates that the lamination is well accomplished and that the charge-discharge data is more reliable in ten laminate cell because of averaging ten individual data. In Fig. 9, the electrolyte was saturated at 40°C, where the capacity was slightly larger than in Fig. 8(a), though the difference is a little. The concentration of the saturated solution at 23°C is very close to 17 m at 25°C and the difference in electrochemical behavior between 17 m (slightly unsaturated) and saturated solutions is very little.

3.9 Role of activated carbon ratios for the energy density of laminate cells

The role of activated carbon ratio in the graphite mixture was examined to determine the energy density of laminate cells using a SS444 foil as a current collector at the cut-off voltage 2.5 V. The
The energy density increased linearly with increasing the activated carbon ratio and reached to be 23 Wh/kg at the activated carbon ratio of 70%. This is a satisfactory result for a simple electric double layer capacitor in view of using commercially available low cost materials.

3.10 Galvanostatic charge-discharge cycles plotted against capacity

Galvanostatic charge-discharge cycles were illustrated for the ten laminate cell using a SS444 foil as a current collector at the cut-off voltage from 2.0 V to 2.5 V as a function of capacity. All data were sampled after 20 cycles.

result is shown in Fig. 10. The energy density increased linearly with increasing the activated carbon ratio and reached to be 23 Wh/kg at the activated carbon ratio of 70%. This is a satisfactory result for a simple electric double layer capacitor in view of using commercially available low cost materials.

3.11 Ti foil as a current collector

In order to avoid the corrosion of current collector, we have tried to use a titanium foil (Hitachi Metals, Ltd.) as a current collector instead of a SS444 foil. Similar experiments as described in Fig. 8 and Fig. 9 were carried out under conditions of maximum applied voltages from 2.0 to 2.75 V. The capacity and the coulombic efficiency are plotted against cycle numbers for each applied voltage as shown in Fig. 12. The discharge capacity increases with increasing the applied voltage up to 2.75 V with the coulombic efficiencies higher than 96%. The result indicates that the Ti foil excels in the corrosion resistance compared with the SS444 foil used.

The temperature dependence was examined for the capacitor using the Ti foil as a current collector under the condition of cut-off voltage 2.5 V and the electric current 1 mA/cm². Galvanostatic charge-discharge cycles were illustrated in Fig. 13 at temperatures ranging from 0 to 60°C. It should be noted in the figure that the IR drop is minimized in all temperatures and the discharge curves start from nearly the same point very close to 2.5 V. The result supports the explanation described above that the IR drop does not always exhibit a guide for an inner resistance.

In Fig. 14, the capacity and the coulombic efficiency for the capacitor using the Ti foil as a current collector are plotted as a function of cycle number at various temperatures from 0 to 60°C. This figure shows that the capacity is kept nearly the same in all temperature region studied. The temperature independence for the present capacity indicates definitely that the charge and discharge processes proceed without diffusion and could be caused in the vicinity of the electrode instead. The result also indicates that the charge and discharge capacities are independent of the electrical conductivity, which changes from 62.0 to 159 mS/cm in the same temperature region in SSPAS. Such a temperature independency in the capacity is reported in the electric double layer capacitor using organic electrolyte. As a result, the electrical conductivity should be significant for the inner resistance of capacitor, but it has no influence on the capacity.
In view of the recovery of regenerating energy, a large electric density should be required. In order to confirm the quantity of electricity, experiments were carried out under the supply of electric current densities up to 50 mA/cm² at 25°C to observe the capacity and the coulombic efficiency. The results are shown in Fig. 15. It can be seen in the figure that the capacity decreases regularly with increasing the electric current density up to 50 mA/cm², however, the coulombic efficiency is 100%. This is quite important considering the recovery of regenerating energy, because the heat generation induced by a large electric current density is of major problem. The electrical loss as well as the inner resistance should contribute to the generation of heat.

3.12 Is the present capacitor able to recover the regenerating energy of automobiles?

A question arises whether the present capacitor stores a considerable amount of energy within few seconds or not. Based on the present data (Fig. 15), we have made a trial product as follows: capacity 0.030 mAh/cm², electric current density 20 mA/cm², and assume to use a current collector 30 cm × 30 cm, thickness 20 µm, numbers of cells 100 (total thickness < 1.0 cm). The total capacity of this unit is 2.7 Ah and it necessitates 1,800 A of the total electric current. The time necessary for the full charge is calculated to be 5.4 s. Although there remain technical problems to disperse the electric current, the present capacitor provides a possibility of charging a required energy within few seconds. Thus, the recovery of regenerating energy necessitates such a larger electric current and, therefore, the high coulombic efficiency as well as the large electrical conductivity is of particular importance in order to control the heat generation. In conclusion, we are convinced of developing the aqueous capacitor using SSPAS for the recovery of regenerating energy of automobiles.

3.13 Comparison of the present capacitor with other capacitors and secondary batteries

Capacitors using organic electrolytes such as PC has been well established and would be functional for the quick charging. However, according to the study by X. Bu, X. Yan et al., the response was not fast enough in case of the charge with the electric current density of 20 A/g. Under the same condition, the capacitor using 17 m NaClO₄ behaved well. The electrical conductivity of PC containing Et₄NBF₄ is about 1/10 of SSPAS and the inner resistance would be larger consequently. A potential danger of burning in organic electrolyte is disadvantageous, though, unlike lithium ion batteries oxidants are not involved in the inside of capacitors, the safety will be kept as far as the seal of container is functioned.

Toshiba announces in the catalog in the lithium ion battery SCiB that a rapid charging enables more than 80% of the total capacity in a minute. Such a rapid charging is surprising for the secondary battery and it is no doubt that the SCiB is an excellent battery. Nevertheless, the charging rate is not enough for the recovery of regenerating energy. Furthermore, a quick charging take place frequently at each time of braking with a large electric current, and such a use is not favorite in general for secondary batteries, where the energy is produced by chemical reactions involving always the heat of reactions. On the other hand, in an electric double layer capacitor, the energy is stored on the surface of electrodes without a chemical reaction and without even the diffusion of ions. Such a phenomenon might be completed rapidly within a second with the least heat of generation.
4. Conclusions

In summary, saturated sodium perchlorate aqueous solution (SSPAS) has a wide potential window over 3 V and is superior to non-aqueous electrolytes with respect to the cost and the safety. A capacitor consisting of laminate cells using SSPAS as an electrolyte, SS444 or Ti foils as a current collector and a mixture of graphite and activated carbon as an active material yields the energy density of 23 Wh/kg, which is large enough to store the recovery energy. This aqueous capacitor accepts a large electric current density with a high coulombic efficiency of nearly 100%, enabling to charge a considerable amount of capacity within few seconds. In conclusion, based on the experimental results, the present capacitor is most feasible at moment for the recovery of regenerating energy of automobiles.

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