Capacitance Degradation in Hydrogel Electrolyte Containing Magnesium-ion Conducting Water-in-Salt Solution

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ABSTRACT

For the purpose of fabrication of novel all-solid-state supercapacitor systems, compatibility of a gel polymer electrolyte consisting of “water-in-salt” aqueous solutions of magnesium bis(trifluoromethane sulfonyl)imide in polyacrylamide matrix was compared with the lithium analogue via symmetric supercapacitor cells. Although the lithium gel electrolyte promotes an irreversible plateau at around 1.5 V during initial charging of a carbon nanofiber based cell, reversible charge–discharge can be up to 2.0 V for an activated carbon based cell. Magnesium gel electrolyte promotes charge–discharge at the first cycle. However, during subsequent cycles, the cells show severe capacitance degradation, probably because of Mg(OH)₂ precipitation at the negative electrode.

Keywords : Hydrogel Electrolyte, Supercapacitor, Water-in-Salt Solution

1. Introduction

All-solid-state capacitors are attractive because of their improved reliability and freedom of cell design. Based on such requirements as ion concentration, high ionic conductivity, and good contact with microporous electrodes for electrolyte, gelification of liquid solution appears to be adequate for an all-(quasi-)solid electrolyte for all-solid-state supercapacitors. Recently, highly concentrated aqueous solutions of lithium fluoroalkylsulfonylimides, so-called “water-in-salt” or “hydrate melt” electrolytes, have been anticipated for use in various electrochemical devices because of their facile handling and widened stable potential range up to 2.8 V. Solutions of this kind are attractive as novel liquid components of gel polymer electrolytes. The resulting gel electrolytes have been used in aqueous lithium-ion batteries and supercapacitors. 5-8 “Water-in-salt”-containing gel electrolyte in supercapacitors presents several important benefits other than a wide potential window, such as non-flammability, low cost of solvents, and high stability. Therefore, hydrated lithium ion, and are expected to provide higher double-layer capacitance because of their small ion size as a mobile ion species. In addition, gel electrolyte of this kind is compatible with asymmetric supercapacitors including ion insertion electrode at either side, which can be selected from various lithium-ion insertion materials. However, to meet needs for resource conservation, the use of lithium must be limited to advanced secondary battery systems with high energy density. The replacement of lithium by magnesium is therefore preferred for use in supercapacitors. Magnesium has been attractive as an alternative host ion species for devices based on insertion-type electrodes. 9,10 Being different from the non-aqueous cases, many magnesium salts are highly soluble in water. They are expected to form stable “water-in-salt” systems by strong hydration to magnesium ions. Magnesium insertion compounds such as V₂O₅ show rather fast insertion kinetics in electrolytes that include some water, 11 exhibiting sustained high-voltage output.

For this preliminary study, concentrated aqueous solutions containing magnesium bis(trifluoromethylsulfonyl)imide [TFSI] salt were applied as a liquid component of gel polymer electrolyte together with poly(acrylamide) (PAAm) matrix cross-linked with bis(methylene acrylamide) (bAAm) in solid-state symmetric supercapacitors. The symmetric capacitor properties consisting of the gel electrolyte have been compared according to the kind of cation with emphasis on the replaceability of lithium by magnesium. Throughout this investigation, the difficulties of magnesium “water-in-salt” gel electrolyte systems for practical application have been elucidated. Herein, the difficulty posed by capacitance degradation is discussed.

2. Experimental

For this study, Mg[TFSI]₂ (Kishida Chemical Co. Ltd., Japan) and LiTFSI (TCI Co. Ltd., Japan) were used without further purification. Distilled water was added to each salt to obtain a corresponding concentrated solution, so that the water content is minimum but the mixture exhibited liquid form at 323 K. The salt–water molar ratios estimated from the gravimetric ratio are dependent with cation, 1:3 for LiTFSI and 1:11 for Mg[TFSI]₂. A hydrogel of a concentrated solution was prepared using the following procedure: acrylamide (0.48 g, AAm; Kanto Chemical Co. Inc., Japan) and N,N'-methylene bisacrylamide (0.04 g, bAAm; Kanto Chemical Co. Inc.) were dissolved in 2 mL of a concentrated solution. Ammonium thiocyanate (Kanto Chemical Co. Inc.) and N,N',N″-tetramethylethylenediamine (Kanto Chemical Co. Inc.) were used together as initiators. After the resultant precursor solution was poured immediately into a Petri dish with a glass filter separator (GF/A; Whatman plc.), it was heated to 360–370 K for 1 h. After AAm and bAAm were polymerized in the solution, a hydrogel a salt-H₂O/PAAm-bAAm confining separator was obtained. The water contents in the hydrogels were reduced to 2 and 4–5 water molecules to one cation, respectively, for the Li and Mg systems. The magnesium “water-in-salt” solution crystallized frequently, even around ambient temperature. Its solution state became stable by the addition of monomers. For that reason, crystallization of hydrated Mg[TFSI]₂ has never adversely affected the preparation process above. For comparison, a conventional electrolyte (Battery Grade, Kishida Chemical Co. Ltd., Japan), 1 mol kg⁻¹ tetraethylammonium tetrafluoroborate (TEABF₄) in propylene carbonate (PC) is included in the same kind of the cell.
The performance of these hydrogels as electrolytes has been estimated using a two-electrode symmetric test cell study including model electrodes. Carbon nano fibers of 20 nm diameter (CNF, VGCF-X; Showa Denko K.K., Japan) and commercially activated carbon with 1324 m$^2$ g$^{-1}$ of specific surface area (AC, KD-PWSP; UES Co. Ltd., Japan) are used as model electrodes. In addition, CNF was used as a conductive agent for the AC electrode. Each electrode was mixed with 10 wt% of poly(tetrafluoroethylene) (PTFE; Daikin Inds. Ltd., Japan), but 5 wt% of CNF for AC in an agate mortar. Then it was pressed into a sheet as a couple of ca. 0.10 g (negative electrode) and ca. 0.13 g (positive electrode) of the composite electrodes included in a cell. The electrode sheet was cut into a 12-mm-diameter circle and was fixed on aluminum mesh with 14 mm diameter. For the AC electrode, the electrode disk attached to aluminum mesh was also confined in a hydrogel. A couple of CNF or AC electrodes together with a hydrogel confining separator were assembled in a two-electrode cell (Hohsen Corp., Japan). Constant-current charge–discharge measurements were taken at 298 K under current density of 0.1 mA cm$^{-2}$ and with cut-off voltages between 2.0 V to 0 V. The assembled cells were stored at 338 K in 1 h before measurement. After 30 cycles of charge–discharge measurement, the AC cell containing Mg[TFSI]$_2$-based hydrogel was disassembled. Then the X-ray diffraction (X’Pert-MRD; Philips Japan Ltd.) was measured for both electrodes, from 10 to 50 degrees at a scan rate of 2.00 degrees s$^{-1}$.

3. Results and Discussion

The stability of all the cell components other than the gel electrolyte can be assured by the charge-discharge performances of the reference cells with TEABF$_4$/PC electrolyte, shown in the Supporting Information. Figures 1(a) and 1(b) present a comparison of the charge–discharge profiles of the CNF cells with concentrated hydrogel electrolytes respectively containing LiTFSI and Mg(TFSI)$_2$. For the CNF cells, composite electrodes were only touched with gel electrolyte without optimization of the interface. Therefore, these cells show considerable interfacial resistance. From the CNF cell results, salient information about the working voltage can be extracted. Cell profiles in Fig. 1 are altered to a marked degree by the electrolytic salt. A long plateau in the profile of the cell containing LiTFSI was observed at around 1.5 V at the first charging process. Further charge–discharge was inhibited by the plateau. This plateau represents electrolyte decomposition. Electrolyte decomposition at such a low voltage contradicts an earlier report stating that concentrated aqueous electrolytes have voltage tolerance as high as 2.8 V by all water molecules coordinated and stabilized for water decomposition. The reason for such low stability is regarded as a certain change on the state of components in the concentrated solution by the gelification. A possible example is the change of water activity by the coexistence with polyacrylamide matrix or electrode surface. By contrast, cells with Mg[TFSI]$_2$-H$_2$O hydrogel show rather typical charge–discharge behavior by the capacitor, with an abrupt voltage change at the start of the charge and discharge processes indicating strong interfacial resistance, and a shorter plateau of by-reaction than that of the Li analogue. In this case, the water decomposition proceeded at a small amount. The cell voltage reached 2.0 V. However, the slopes of the charge–discharge curves increase considerably, indicating severe capacitance degradation in subsequent cycles.

The charge–discharge profiles at selected cycles for symmetric cells with the AC electrodes are presented in Figs. 1(c) and 1(d). In addition, the cycle performances of the AC-based symmetric cells
containing various electrolytes are summarized in Fig. 1(e). The specific capacitances for these cells with LiTFSI and Mg[TFSI]₂ at initial cycle were found to be 112 and 96 F per mass unit for a single and partially crystallized polyacrylamide can show di LEWIS,16 but another peak at 26° indicates amorphous carbon and peaks (ca. 80 F g⁻¹) might overlap a peak shown by aluminum. This latter peak is absent from the di ffraction patterns of electrodes of activated carbon/Mg[TFSI]₂·H₂O symmetric capacitor cell after charge-discharge measurements.

This result indicates that capacitance decay is a characteristic of the Mg[TFSI]₂·H₂O hydrogel electrolyte. The change in the AC electrodes during charge-discharge and the ex situ X-ray diffraction measurements of the AC electrodes from a disassembled cell have been found. The X-ray diffraction patterns of the AC positive and negative electrodes after cycling are portrayed in Fig. 2. Regarding the di ffraction pattern of the positive electrode, several peaks are observable in the whole region between 10° and 50°. The origin of these peaks is not yet identified because measurements were conducted using an unwashed sample. The Mg[TFSI]₂; crystallized (from the similarity to LiTFSI) by drying and partially crystallized polycrylamide can show di ffraction peaks in this region. By contrast, the negative electrode after cycling shows fewer peaks, with five small peaks around 16°-21° in addition to a broad peak around 26° indicating amorphous carbon and peaks at 38° and 44° attributed to the aluminum current collector. The peak at 17° was observed corresponding to Mg(OH)₂, although another peak at 38° might overlap a peak shown by aluminum. This latter peak is absent from the di ffraction pattern of the positive electrode. This result suggests that water reduction occurred on the surface of the negative electrode under high voltage charging, resulting in hydrogen evolution. Then the concentration of hydroxyl ion at the electrolyte near the negative electrode, as indicated by Dubouis et al., increases to provide deposition of Mg(OH)₂. The deposited Mg(OH)₂ may enclose the pores of the AC negative electrode. It may finally reduce the cell capacitance by cycles. Electrolyte decomposition also causes a lack of water. Thereby, Mg[TFSI]₂ deposited at the positive electrode side inhibits further electrolyte decomposition, even with the CNF electrode. According to this hypothesis, the capacitance fading which occurs over many cycles is preventable by the application of a redox negative electrode, which has redox potential greater than that of hydrogen evolution. Additionally, the water activity might be different in the Mg[TFSI]₂·H₂O gel electrolyte from the corresponding liquid electrolyte. Further study will be undertaken to examine the construction of a 2V-class capacitor cell containing magnesium salt water-in-salt gel electrolyte with selection of a proper redox negative electrode or through inhibition of Mg(OH)₂ formation.

Supporting Information

The Supporting Information is available on the website at DOI: https://doi.org/10.5796/electrochemistry.20-00117.

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