Journal of Electroanalytical Chemistry 826 (2018) 60–64

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

Electrochemical properties of lead fluoride electrode in fluoride shuttle battery

Hiroaki Konishi[a,*], Taketoshi Minato[b,**], Takeshi Abe[c,**], Zempachi Ogumi[a]

[a] Office of Society-Academia Collaboration for Innovation, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan
[b] Office of Society-Academia Collaboration for Innovation, Kyoto University, Katsura, Nishikyo, Kyoto 615-8510, Japan
[c] Graduate School of Global Environmental Studies, Kyoto University, Katsura, Nishikyo, Kyoto 615-8510, Japan

ARTICLE INFO

Keywords:
Fluoride shuttle battery
Lead fluoride
Electrolyte
XRD
AAS

ABSTRACT

Recently, the reversible discharge and charge reaction of BiF_3 electrode for fluoride shuttle battery (FSB) that can be used as a promising candidate for next-generation battery are observed using a liquid-based electrolyte. In this study, we investigate the electrochemical performance of PbF_2 as an active material for the FSB. To increase the electronic conductivity, the PbF_2 was mixed with carbon, and the composite material between PbF_2 and carbon, PbF_2/C, is formed. High discharge and charge capacities are obtained for PbF_2/C during the first cycle. Although the discharge and charge capacities gradually decreased, the discharge and charge reactions occurred in the second and third cycles. To confirm the progress of the discharge and charge reactions, the crystal structure change of the active material during discharging and charging in the first and second cycles is evaluated using X-ray diffraction (XRD). From the XRD results, the formation of Pb and PbF_2 during discharging and charging can be confirmed, indicating that the discharge ($PbF_2 + 2e^- \rightarrow Pb + 2F^-$) and charge ($Pb + 2F^- \rightarrow PbF_2 + 2e^-$) reactions progress in both the first and second cycles.

1. Introduction

Lithium-ion batteries (LIBs) are extensively used as secondary batteries for many electronic devices [1–3]. To increase the use of secondary batteries, many research institutions have investigated a variety of next-generation high-energy-density batteries such as sodium, magnesium, potassium, lithium/oxygen batteries [4–7]. Recently, batteries that utilize anion migration to perform the electrochemical reaction have been developed [8–15]. In 2011, Reddy et al. reported a new all-solid battery which utilizes the migration of fluoride ions [8]. For this battery, the metal fluoride and metal were used as the active material, and fluoride ions migrated between metal fluoride and metal through a solid electrolyte. Since this study was conducted, the progress of electrochemical reaction of several metal fluorides using a solid electrolyte has been reported [8–11]. Furthermore, the battery using a liquid-based electrolyte has also been researched [12,13]. Our group has devoted attention to a battery that utilizes the fluoride-ion shuttling in a liquid-based electrolyte [16,17]. However, the supporting electrolyte salt such as cesium fluoride (CsF) hardly dissolved in the organic solvent [17]. To increase the solubility of CsF in the organic solvent, anion acceptor (AA) was added in the organic solvent [17]. Using the liquid-based electrolyte comprising organic solvent (bis[2-(2-methoxyethoxy)ethyl] ether (tetraglyme: G4)), supporting electrolyte salt (CsF), and AA (fluorobis(2,4,6-trimethylphenyl)borane (FBTMPhB)), the discharge and charge reactions of BiF_3 successfully progressed, and the progress of both the reactions were confirmed using X-ray diffraction (XRD). Using the XRD results, the discharge reaction of BiF_3 was observed to completely progress; however, the charge reaction progressed partially [17]. To obtain high capacities during both discharging and charging, high ionic and electronic conductivities are required for the active material. The PbF_2-based compounds exhibit fluoride ion conductivity [18–21]; therefore, PbF_2 was selected as an active material for the fluoride shuttle battery (FSB). It has been reported that the high adhesion state with carbon improved the discharge and charge capacities of metal fluorides for the active materials of LIBs due to the increased electronic conductivity [22–32]. This method can be used for the active material of the FSB. Thus, in the current study, the composite electrode of PbF_2 and carbon, PbF_2/C, was formed using a ball mill. The electrochemical performance of PbF_2/C was evaluated using the electrolyte comprising of G4, CsF, and FBTMPhB. Furthermore, to confirm the progress of the discharge and charge reactions, the crystal structure change of the active material was analyzed using XRD.

---

* Correspondence to: H. Konishi, Research & Development Group, Hitachi Ltd., Hitachi, Ibaraki 319-1292, Japan.
** Corresponding authors.
E-mail addresses: hiroaki.konishi.yj@hitachi.com (H. Konishi), minato.taketoshi.5x@kyoto-u.ac.jp (T. Minato), abe@elech.kuic.kyoto-u.ac.jp (T. Abe).

https://doi.org/10.1016/j.jelechem.2018.08.027
Received 10 May 2018; Received in revised form 19 August 2018; Accepted 20 August 2018

2. Experimental

2.1. Preparation of the electrolyte

The CsF (Tokyo Chemical Industry Co., Ltd), FBTMPhB (Tokyo Chemical Industry Co., Ltd), and G4 (KISHIDA CHEMICAL Co., Ltd) were used as the supporting electrolyte salt, the AA, and the organic solvent, respectively. The G4 containing 0.45 mol dm^{-3} CsF and 0.5 mol dm^{-3} FBTMPhB was used as the electrolyte. The electrolyte was prepared in a glove box under high purity argon.

2.2. Preparation of the active material

The PbF_2 (Aldrich) was used as the active material. This was pulverized for 1 h in a planetary ball mill (FRITSCH PULVERISETTE 7) at 1100 rpm, and was then 80 wt% pulverized PbF_2; further, 20 wt% acetylene black (AB) was mixed for 1 h in the planetary ball mill at 1100 rpm to produce PbF_2/C. The PbF_2 and AB were sealed in the planetary ball mill under a high purity argon atmosphere.

2.3. Characterization of the active material

For PbF_2/C, the crystal structure, particle configuration, and solubility in the electrolyte were investigated by XRD, scanning electron microscopy (SEM), and atomic absorption spectrometry (AAS). The XRD measurements were performed with a Rigaku Smartlab. XRD patterns were recorded in the 2θ range from 20° to 70° using a Rigaku diffractometer with Cu Kα radiation (λ = 1.54 Å). The SEM measurements were performed on a HITACHI SU6600 instrument, and the energy of the incident electrons was 20 keV. The AAS measurements were performed using a polarized Zeeman atomic absorption spectrophotometer (Hitachi).

2.4. Characterization of electrolyte

To evaluate the stability of the electrolyte during cycling, cyclic voltammetry (CV) was conducted using a three-electrode electrochemical cell (EC FRONTIER CO., Ltd. VB7) comprising a platinum foil as the working electrode, a platinum mesh as the counter electrode, and a silver rod immersed in acetonitrile containing 0.1 mol dm^{-3} silver nitrate and 0.1 mol dm^{-3} tetraethylammonium perchlorate as the reference electrode (0.587 V vs. standard hydrogen electrode) [33]. The CV of the prepared electrolyte was performed at room temperature using a multipotentiostat (Biologic VMP-300) over a −4.0 to 2.0 V (vs. ref.) potential range at a sweep rate of 0.1 mV s^{-1} during the three cycles. The assembly of electrochemical call and CV measurements were performed in a glove box filled with high purity argon.

2.5. Electrochemical performance of PbF_2/C

Firstly, the PbF_2/C, AB, and polyvinylidene difluoride (75: 10: 15 wt %) were mixed, and *N*-methyl-2-pyrrolidone (NMP) was added. The resulting slurry was coated on an Al current collector, and the NMP was evaporated at 110 °C. The discharge and charge capacities of the PbF_2/C electrode were measured using a three-electrode electrochemical cell consisting of a PbF_2/C electrode as the working electrode, a platinum mesh as the counter electrode, and a silver rod immersed in acetonitrile containing 0.1 mol dm^{-3} silver nitrate and 0.1 mol dm^{-3} tetraethylammonium perchlorate as the reference electrode. The charge and discharge measurements were performed using a multipotentiostat (Biologic VMP-300) within a potential range from −2.0 to −0.6 V (vs. ref.) at 0.025C (~20 μA cm^{-2}) and room temperature in an argon atmosphere. The specific capacity was obtained by dividing the capacity with the weight of the active material (PbF_2).

2.6. Crystal structure of PbF_2/C during discharging and charging

The crystal structures of PbF_2/C during discharging and charging in the first and second cycles were evaluated using XRD. After the PbF_2/C electrodes were discharged and charged, they were washed with G4 followed by dimethyl carbonate to eliminate the residual electrolyte. The XRD patterns were recorded in the 2θ range from 25° to 45°.

2.7. Dissolution amount of Pb in the electrolyte during discharging and charging

The dissolution amount of Pb in the electrolyte in the first fully discharged and charged states was measured by AAS. After the PbF_2/C electrode was discharged and charged, the electrochemical cell was disassembled, and the electrolyte was recovered from the cell. The concentration of Pb in the electrolyte was measured.

3. Results and discussions

3.1. Characterization of PbF_2/C

The XRD pattern of PbF_2/C powder is illustrated in Fig. 1. All the diffraction peaks are assigned to the cubic phase with space group *Fm*3*m*. The SEM images of PbF_2 and PbF_2/C powders are depicted in Fig. 2. The particle size of PbF_2 (before mixing with AB) is 0.5–2 μm (Fig. 2(a)). After mixing with AB, smaller particles of AB are observed on the PbF_2 particle surfaces (Fig. 2(b)). This indicates that AB particles are adhered to the surface of the PbF_2 particles after mixing.

3.2. Stability of electrolyte during the cycling

To evaluate the stability of the electrolyte during cycling, CV was performed. The CVs of the prepared electrolyte during the first, second, and third cycles are depicted in Fig. 3. There was a large reduction peak below −2.2 V (vs. ref.) and a small oxidation peak between −0.3 and 0.5 V (vs. ref.) during the first cycle. The shapes of the CVs during the second and third cycles are similar to that during the first cycle. This indicates that the prepared electrolyte could be used repeatedly between −2.2 and −0.3 V (vs. ref.).

3.3. Electrochemical performance of PbF_2/C

The discharge and charge curves of PbF_2/C are depicted in Fig. 4.

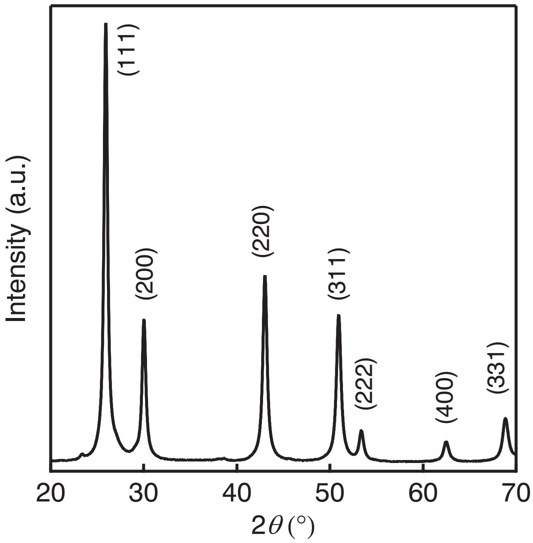

Fig. 1. XRD pattern of the PbF_2/C powder.