

Short communication

Discharge characteristics of chemically prepared MnO_2 and electrolytic MnO_2 in non-aqueous electrolytes

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Abstract

The discharge performance of chemically prepared MnO_2 (CMD) and electrolytic MnO_2 (EMD) is investigated in various electrolytes. LiPF_6 , LiCF_3SO_3 , and LiBF_4 are used as lithium salts in a mixed solvent of ethylene carbonate, propylene carbonate, and 1,2-dimethoxyethane (DME). The size and crystal structure of MnO_2 particles is observed by scanning electron microscope and X-ray diffraction, respectively. The particle size of CMD is smaller than that of EMD, but the crystal structures of the two materials are similar. The concentration of dissolved manganese ions from CMD and EMD particles is 148 and 23 mg l^{-1} in the same electrolyte, respectively. The interfacial electrochemistry of test cells is analyzed by impedance spectroscopy. The discharge performance is poor in the electrolyte containing LiCF_3SO_3 salt. The specific discharge capacity of CMD is superior to that of EMD at high discharge rate.

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1. Introduction

Lithium–manganese dioxide (Li–MnO_2) batteries use MnO_2 as a cathode active material. This material has been traditionally employed in other alkaline manganese batteries. Ikeda et al. [1,2] succeeded in commercializing a Li–MnO_2 battery in 1975. The Li–MnO_2 battery has various advantages such as high specific energy, excellent discharge characteristics, no gas evolution, and good storage characteristics [3]. In addition, since this battery uses an organic solvent with a low freezing point, it operates over a wide temperature range.

MnO_2 active materials are produced by chemical and electrochemical methods. In the former case, the material is called ‘chemically prepared MnO_2 ’ (CMD) and the latter is called ‘electrolytic MnO_2 ’ (EMD). These MnO_2 materials must be anhydrous and have a suitable structure for intercalation of lithium ions for good performance characteristics. The crystal structure and physical properties of CMD are different from those of EMD [4]. CMD has a pyrolusite structure ($\beta\text{-MnO}_2$). This is the simplest structure in the

various kinds of MnO_2 and the chemical composition is very close to the ideal ratio of $\text{Mn}:\text{O} = 1:2$. The crystal structure of EMD is $\gamma\text{-MnO}_2$ and has a more open structure and is usually less crystalline. EMD exists in various other forms (α , δ , and others) when containing foreign cations [5].

Recently, various electrolytes (lithium salts and solvents) for Li–MnO_2 batteries were investigated to improve the discharge performance [6]. Generally, 1 M LiClO_4 salt and a mixed solvent of propylene carbonate (PC) and 1,2-dimethoxyethane (DME) has been used in Li–MnO_2 primary batteries. The discharge reaction of the Li–MnO_2 battery depends on the electrolyte type. At high rates of discharge, the capacity and voltage profile are dependent on the ionic conductivity of the electrolyte and the interfacial resistance between the electrolyte and the electrode. The interfacial resistance results from a decomposition reaction between the electrolyte and the lithium electrode. Therefore, a proper lithium salt is an important factor to ensure good discharge performance in lithium battery.

In this communication, the electrochemical characteristics of various lithium salts in a mixed solvent to improve the discharge performance of a Li–MnO_2 battery based on CMD and EMD.

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2. Experimental

MnO₂ cathode active materials were chemically prepared manganese dioxide (CMD) and electrolytic manganese dioxide (EMD). These materials were purchased and used without further treatment. The positive electrodes (cathodes) were composed of 86 wt.% active material, 8 wt.% acetylene black conductor, and 6 wt.% poly(vinylidene fluoride) binder. The battery construction is shown in Fig. 1. This flat-type battery is composed of a cathode, a lithium negative electrode (anode), and a poly(propylene) separator between. The assembly was enveloped with aluminum plastic bag and sealed by vacuum sealer. Various electrolytes were used to investigate the discharge performance; 1 mol LiPF₆, 1 mol LiCF₃SO₃, and 1 mol LiBF₄ were dissolved in a mixed solvent of EC:PC:DME (25:25:50 vol.%).

The assembled battery was discharged at constant current by means of a Maccor battery tester. Analysis of the impedance spectra of Li–MnO₂ cells was performed with a Zhanher im6 instrument.

MnO₂ active materials were examined in a scanning electron microscope (SEM; Hitachi, S-4200), and the crystal structure of MnO₂ materials was analyzed by X-ray diffraction (XRD; Rint/Dmax-2500, Rigaku). The chemical stability of the MnO₂ particles in the electrolyte was determined by atomic absorption spectroscopy (AAS; spectra AA 800 series, Varian).

3. Results and discussion

3.1. Size of MnO₂ particles

Scanning electron micrographs of each type of MnO₂ particle are shown in Fig. 2. The EMD particles are relatively coarse and are larger than the CMD particles. The CMD particles are spherical with a diameter of about 10–20 μm. Since most of the electrochemical reaction takes place on the surface of the particles, EMD particles may be electrochemically less active than CMD particles.

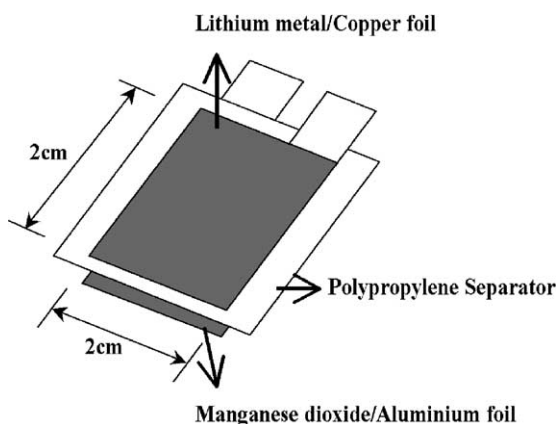


Fig. 1. Schematic construction of Li–MnO₂ cell.

3.2. Crystal structure of MnO₂ particles

The X-ray diffraction patterns of each type of MnO₂ particle are given in Fig. 3. These particles have broad peaks that suggest an undeveloped crystal structure. The crystal structure of CMD is similar to that of EMD. Therefore, it is considered that these compounds have a similar tunnel structure to intercalate lithium ion. The transport properties of each structure for lithium ions, as well as lithiated compounds such as various lithium salts, are important for the performance of battery. During electrochemical discharge, the lithium is intercalated in the MnO₂ structure. This reaction is irreversible at high current density because of a significant change in the unit cell parameters. Thus, attention is focused on the specific discharge capacity rather than on the reversibility of the active materials.

3.3. Solubility of MnO₂ particles

Two grams of MnO₂ particles was mixed and stored in 15 ml of 1 M LiBF₄/EC:PC:DME electrolyte in order to determine the solubility of MnO₂. After 10 days, the solution

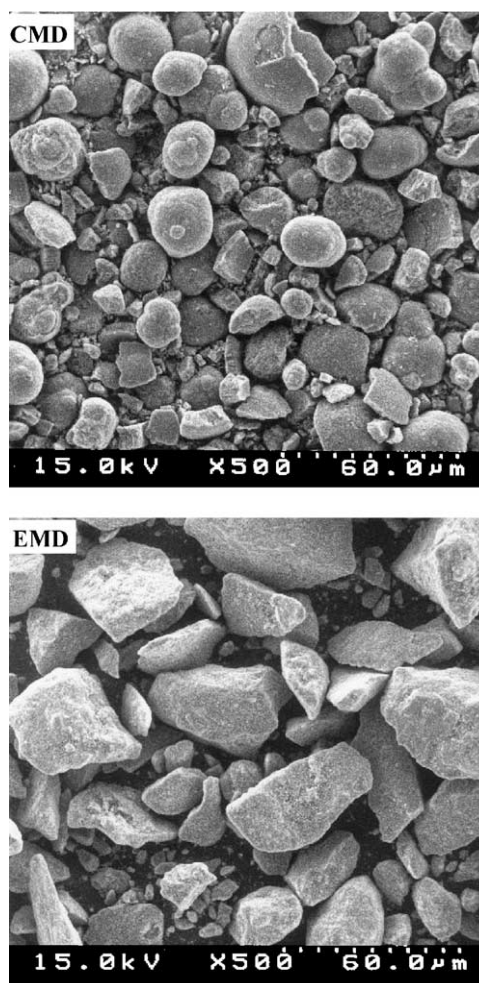


Fig. 2. Scanning electron micrographs of manganese dioxide particles.

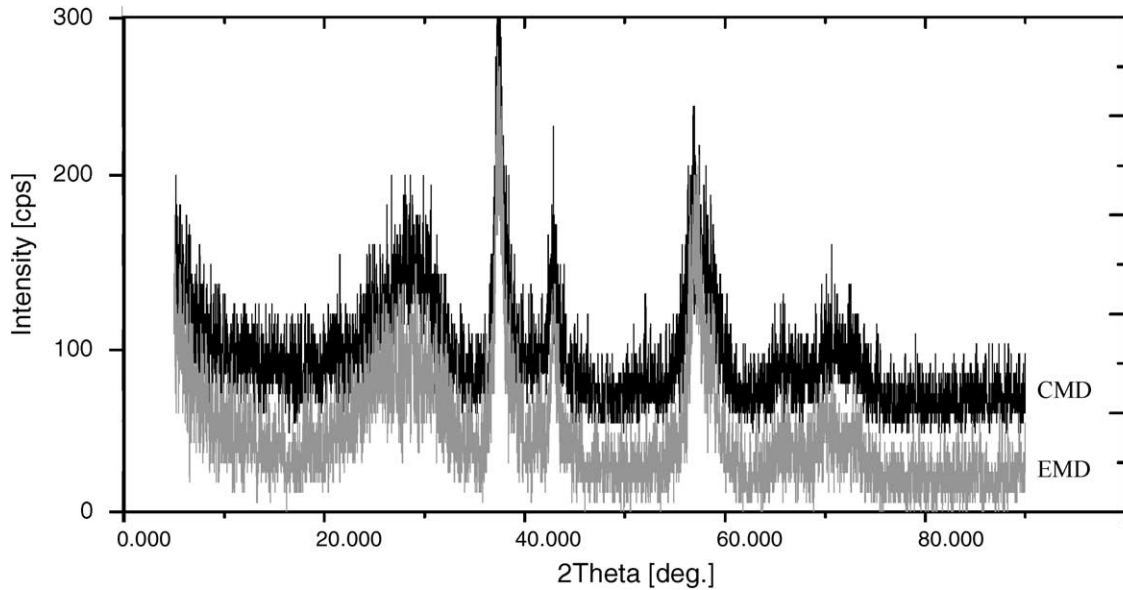


Fig. 3. XRD patterns of CMD and EMD particles.

was filtered and analyzed by means of AAS. The dissolved manganese ion concentration of CMD and EMD particles is 148 and 23 mg l^{-1} , respectively. CMD is more stable thermodynamically than EMD because it has a perfect stoichiometry structure. Since the size of CMD is much smaller than that of EMD, however, the surface area of CMD particles is exposed easily to the electrolyte.

3.4. Impedance characteristics of test cells

The impedance spectrum of test cells based on CMD in various electrolytes after a 1-day storage at room tempera-

ture is presented in Fig. 4. The diameter of the semicircles corresponds to the interfacial resistance of the test cells. The impedance value of the Li–MnO₂ cell containing LiCF₃SO₃ is larger than that of cells containing LiPF₆ or LiBF₄. It is considered that the increase in impedance is caused by an increase in the interfacial resistance between the lithium electrode and the electrolyte. This interfacial resistance arises from a decomposition reaction between the electrolyte and lithium electrode. The lithium, anode is always covered with a passive layer called the solid electrolyte interphase (SEI). The chemical composition and electrochemical properties of this layer are still not well

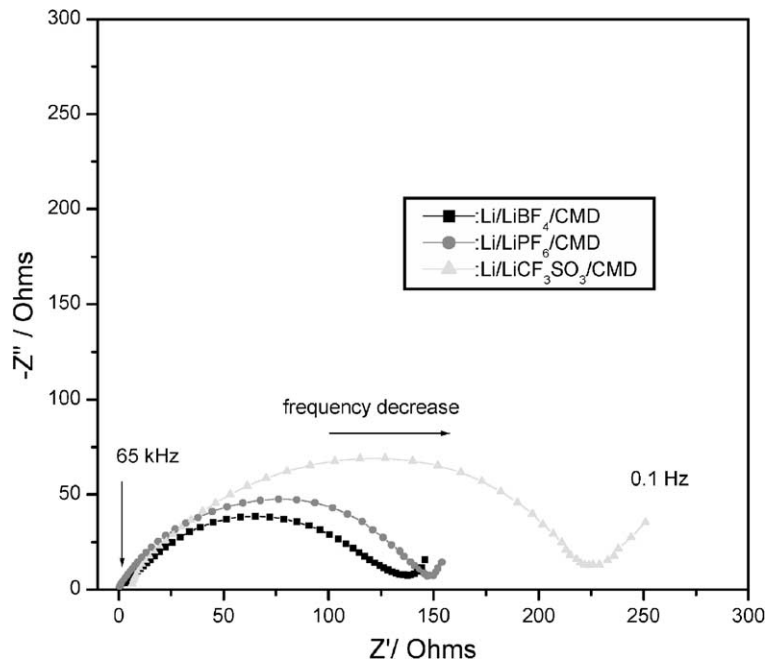


Fig. 4. Impedance spectra of Li–MnO₂ cells based on CMD.

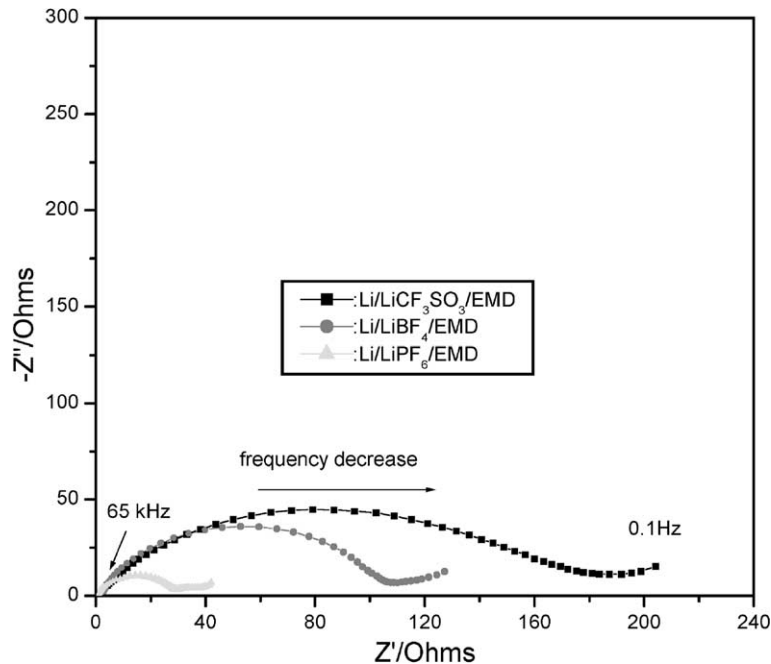


Fig. 5. Impedance spectra of Li-MnO₂ cells based on EMD.

understood. Kanamura et al. [7] studied the chemical composition of surface films deposited on a nickel substrate in various electrolytes. They found that the composition depends on the type of lithium salt. In the work reported here, it is considered that LiCF₃SO₃ is more reactive to the lithium electrode.

The impedance spectra of test cells based on EMD in various electrolytes are given in Fig. 5. The interfacial resistance formed in these cells is lower than that formed in CMD cells. This phenomenon may be attributed to the degree of solubility of MnO₂ particles in the same electrolytes. The solubility of CMD is higher than that of EMD, as discussed above. The dissolved manganese ion may be deposited on a lithium electrode. This effect increases the interfacial resistance. From elemental analysis, Nohma et al. [8] reported that manganese peaks appeared on the lithium electrode surface. Therefore, there may be interactions between lithium salts and the MnO₂.

3.5. Discharge characteristics of test cells

The specific discharge capacity of test cells based on CMD in various electrolytes at the C/5 rate is shown in Fig. 6. The use of LiBF₄ as a lithium salt yields the highest discharge capacity, viz. 210 mA h g⁻¹. The operating voltage of this cell is approximately 2.78 V. It is considered that this cell has good high-rate discharge characteristics due to its low interfacial resistance, as discussed above. In addition, these active materials are thought to have low crystallinity. Murphy et al. [9] reported that crystalline β-MnO₂ has a low discharge capacity of 62 mA h g⁻¹. On the other hand, β-MnO₂ materials with low crystallinity yield more than

200 mA h g⁻¹ [10]. Since the particle size of EMD is coarser and larger, the specific discharge capacity of EMD is usually lower than that of CMD at high discharge rate, as shown in Fig. 7. If the size of the cathode active material is small, the rate of lithium ion intercalation into the cathode is fast, even at high rate. EMD particles have less space to intercalate lithium ions compared with CMD particles due to the size effect.

Even though EMD particle has a high performance from an electrochemical point of view, it must be milled before use to improve the discharge characteristics.

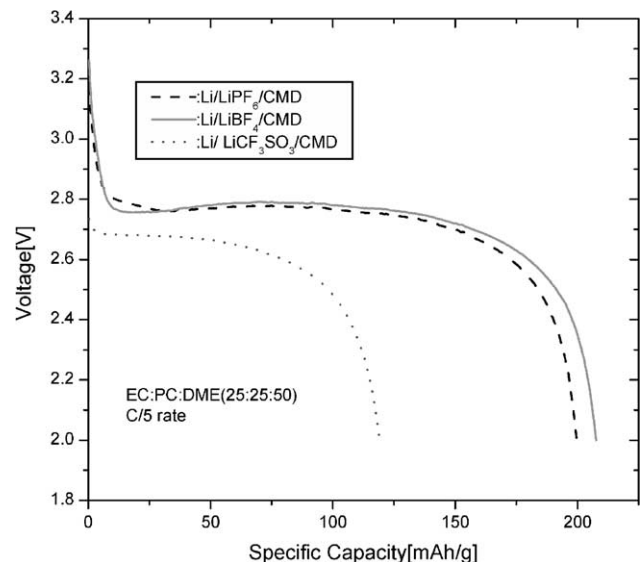


Fig. 6. Discharge characteristics of Li-MnO₂ cells based on CMD.

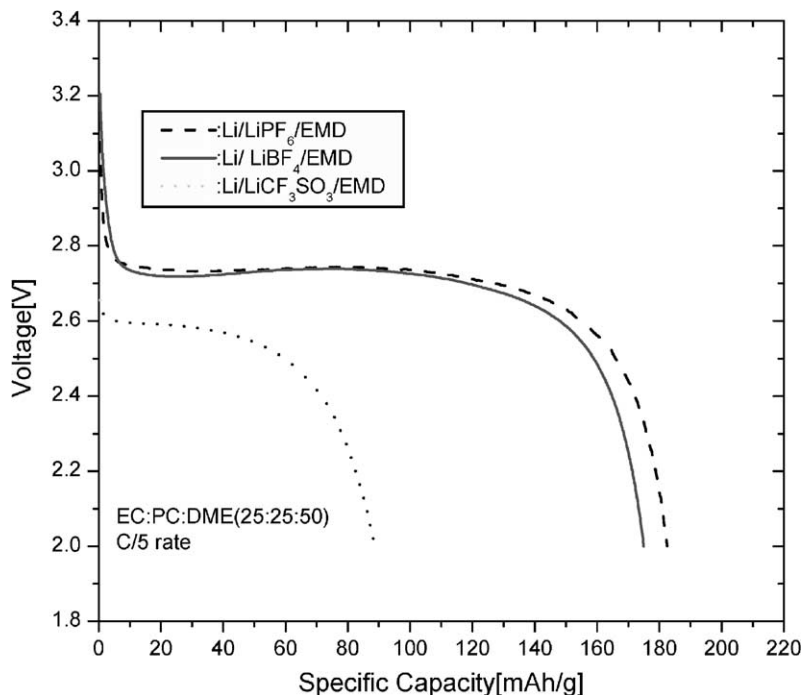


Fig. 7. Discharge characteristics of Li-MnO₂ cells based on EMD.

4. Conclusions

EMD particles are larger than CMD particles, but the XRD patterns of each type of particle are similar. The content of dissolved manganese ions from CMD and EMD particles is 148 and 23 mg l⁻¹, respectively, in an electrolyte based on 1 M LiBF₄ in a mixed solvent of EC:PC:DME. The interfacial resistance of a Li-MnO₂ cell containing LiCF₃SO₃ is higher than that of Li-MnO₂ cells containing other lithium salts. When CMD is used as a cathode, LiBF₄ gives a large capacity than any other lithium salt. When EMD is used as a cathode, LiPF₆ exhibits the largest capacity among the lithium salts.

Acknowledgements

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