



Improved LiMn₂O₄/Graphite Li-Ion Cells at 55°C

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Sodium phosphate additives and mixed electrolytes of Li(C₂F₅SO₂)₂N (LiBETI) and LiPF₆ were examined to improve cycle performances of Li_{1.04}Mn_{1.96}O₄/graphite cells at high temperatures. The cycle performance of those cells exceeded 80% at 100 cycles at 55°C in an optimum combination of a 0.975 M LiBETI and 0.025 M LiPF₆/ethylene carbonate (EC):dimethylcarbonate (DMC) (1:2) electrolyte solution containing 5% of Na₄P₂O₇ or 5% of Na₅P₃O₁₀ additive. Such a cycle performance is considered to fulfill the requirement for practical use.

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Lithium-ion batteries are currently and widely used in portable devices such as mobile phones because they have some advantages over other kinds of batteries, such as high potentials and highly specific energies. Meanwhile, demand for lithium-ion batteries in large sizes has increased for use in plausible electric and hybrid vehicles, especially the plug-in hybrid vehicles.¹ For such applications, good cycle performance, high discharge rate, safety measures, environmental friendliness, and cost performance are particularly required. In these respects, a spinel-type lithium manganese oxide, LiMn₂O₄, is considered more favorable as a positive electrode than conventionally used LiCoO₂ as it is safer, richer in natural resources, and more permissible. However, a Li-ion battery using LiMn₂O₄ as a positive electrode has a disadvantage in that it deteriorates badly at high temperatures in combination with carbon negative electrode. This has been attributed to the severe capacity loss of the carbon negative electrode due to the deposition of Mn ions dissolved out of the lithium manganese oxide.²

There are many studies to improve the capacity fading of LiMn₂O₄ electrodes against Li negative electrodes.³ However, only a little work explaining the causes of the deterioration is currently available among the papers published concerning cells of LiMn₂O₄ and carbon electrodes, and the improvement of such deterioration has not been achieved sufficiently.⁴ We have already reported that Mn solubility was decreased by the addition of Na₃PO₄ to the positive electrode and that this lead to better storage performance of the LiMn₂O₄/graphite cell, while a better cycle performance had not been obtained in such cells.⁵

In the present study, we examined the effects of sodium phosphate additives to both lithium manganese oxide electrodes and molecular anion electrolytes such as Li(C₂F₅SO₂)₂N (LiBETI). They are supposed to suppress acid formation from the hydrolysis, which causes Mn dissolution. Then the high-temperature performance would be improved for the Li_{1.04}Mn_{1.96}O₄/graphite Li-ion cell.

Experimental

Materials.—The positive material used here is the typical spinel-type lithium manganese oxide which was supplied by Nippon Metals and Chemicals (Tokyo, Japan) and its chemical composition is Li_{1.04}Mn_{1.96}O₄. The crystal structure is indexed to a cubic system (the space group *Fd3m*) with lattice parameters *a*₀, 8.2341 Å, and the initial discharge capacity is 119 mAh/g at a 1C rate in the range from 3.5 to 4.5 V. Additives, Na₃PO₄ and Na₂HPO₄, to the positive electrode were available from Kishida (Osaka, Japan) and Nakarai (Tokyo, Japan), respectively. Similar additives of Na₄P₂O₇, Na₅P₃O₁₀, and (NaPO₃)_{*n*} were purchased from Wako (Tokyo, Japan). The 2:1 mixture (CB-2) of acetylene black binder to poly(tetrafluoroethylene) (PTFE) and mesophase-pitch-based carbon

fiber (MCF) as the negative material were available from Soei Tsusho (Osaka, Japan) and Petoka (Tokyo, Japan), respectively, and poly(vinylidene fluoride) (PVDF) and *N*-methyl-2-pyrrolidinone were supplied by Kureha Chemical Industry (Tokyo, Japan) and Kanto Chemical (Tokyo, Japan), respectively. The test cells (CR2032) were purchased from Housen (Osaka, Japan).

The 1:2 solvent mixtures of ethylene carbonate (EC) to dimethyl carbonate (DMC) with 1 M LiPF₆ and LiBETI dissolved were given by Mitsui Chemical (Tokyo, Japan) and contained less than 10 ppm of H₂O. They were mixed at appropriate ratios.

Electrochemical cells.—The lithium manganese oxide positive electrode was prepared in a conventional way; the mixture of two-thirds of the lithium manganese oxide powder and one-third of CB-2 was pressed carefully at 200 kg/cm² to make it into a disk for the positive electrode of a cell and was then dried at 150°C for 6 h.

The graphite negative electrodes were prepared by mixing MCF and 7 wt % PVDF with *N*-methyl-2-pyrrolidinone until a homogeneous paste was obtained, spreading the carbon paste on Cu foils, and evaporating to dryness under vacuum for 10 h at 150°C. Performance tests were done on a coin-type cell (CR-2032).

All processes of assembling and dismantling the cells were carried out in an argon atmosphere in a glove box (Vacuum Atmospheres Co., California, USA).

Measurements.—Elemental analyses of samples were made with a fluorescent X-ray spectrometric method. The contents of Mn on Li or graphite negative electrodes were measured with the conventional method⁶ using a Hitachi 180-50 atomic absorption spectrophotometer.

Storage experiments are as follows; the cell with a Li negative electrode as a counter electrode was charged up to 4.5 V and discharged down to 3.5 V to measure its discharge capacity. It was cycled two times and charged up 20% state of charge (SOC) and then stored galvanostatically at 55°C for a week at the constant potential maintained using a Nagano BTS-2004. After storage, the cell was charged up to 4.5 V and discharged down to 3.5 V to measure its discharge capacity at room temperature. In the graphite electrode, a cell was prepared to be capacity ratio 10:3 = positive electrode/negative electrode and charged up to 1C and discharged down to 3.3 V. It was cycled three times to measure its discharge capacity and charged up to 1C and then stored galvanostatically at 55°C for a week at the constant potential maintained using a Nagano BTS-2004. After storage, the cell was discharged down to 3.3 V to measure its discharge capacity at room temperature. After the storage experiment was finished, each cell was dismantled and a negative electrode in the cell was taken out to measure Mn contents.

For cycle experiments, a cell was prepared to have the capacity ratio of 10:11 of positive electrode to graphite electrode and charged up to 4.2 V and discharged down to 2.5 V. It was cycled in the 2.5–4.2 V range at 55°C using a Nagano BTS-2004. At the 101st

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Table I. Capacity retentions and Mn dissolutions for $\text{Li}_{1.04}\text{Mn}_{1.96}\text{O}_4/\text{Li}$ or graphite cells with Na_3PO_4 as an additive after storage at 55°C for a week. The electrolyte is 1 M $\text{LiPF}_6/\text{EC}:\text{DMC}$ (1:2).

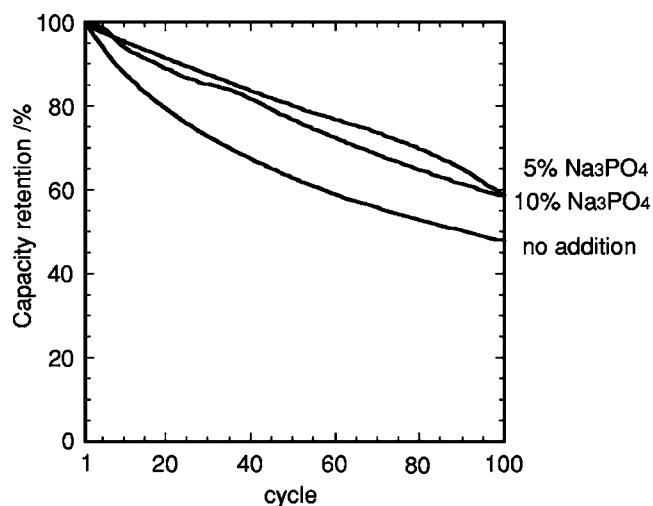
| Additives | No addition | 5% Na_3PO_4 | No addition | 5% Na_3PO_4 | 10% Na_3PO_4 |
|------------------------|-------------|-----------------------------|-------------|-----------------------------|------------------------------|
| Negative electrode | Li | Li | Graphite | Graphite | Graphite |
| Capacity retention (%) | 90 | 89 | 47 | 69 | 66 |
| Mn dissolution (%) | 0.58 | 0.13 | 0.28 | 0.030 | 0.024 |

cycle, each cell was dismantled and a negative electrode in the cell was taken out to measure Mn content. The cycle tests were run three times.

Results and Discussion

Table I shows the results of storage performance at 55°C for the cell containing Na_3PO_4 as an additive, where $\text{Li}_{1.04}\text{Mn}_{1.96}\text{O}_4$ is a positive electrode and Li or graphite is a negative electrode. The storage performances keep almost the same capacity retentions of 90 and 89% for the cells containing 0 and 5% of Na_3PO_4 as additives with Li negative electrodes, respectively. The Mn dissolutions decrease to 0.13% for a 5% Na_3PO_4 additive case from 0.58% for 0% Na_3PO_4 . Although 5% of Na_3PO_4 addition leads to less Mn dissolution, storage performances remain almost the same for both cells with the Li negative electrode. But, for the case using the graphite negative electrodes, the lower storage performance, 47%, is observed in contrast to 90% for the Li counter electrode. From this, it follows that the degradation of the graphite electrode is one of the dominant factors of the capacity fading in the cell at high temperature. The addition of 5 and 10% Na_3PO_4 leads to 69 and 66% of the storage performances, respectively, and their capacity losses decrease. The extents of Mn dissolution decrease markedly to 0.03 and 0.02% for both cells from 0.28% of the cell without additives. Thus, the addition of Na_3PO_4 is effective for the improvement of high-temperature storage performance in the cell with LiMn_2O_4 and graphite as a positive and negative electrode, respectively.

Figure 1 shows the results of the cycle performance for the cells with graphite electrodes at 55°C . At the 100th cycle, the capacity retentions, defined as (1st discharge capacity)/(the discharge capacity at the 100th cycle), are 48, 59, and 58% for 0, 5, and 10% of Na_3PO_4 addition, respectively, and the capacity losses are improved about only 10% by their addition. Thus, the contribution of their additives to the improvement is smaller than that on the storage performance. In addition, for 5 and 10% Na_3PO_4 additive, their capacity retention curves are not smoother but more unstable.

**Figure 1.** Cycle performance for $\text{Li}_{1.04}\text{Mn}_{1.96}\text{O}_4/\text{graphite}$ cells with Na_3PO_4 as an additive at 55°C . The electrolyte is 1 M $\text{LiPF}_6/\text{EC}:\text{DMC}$ (1:2).

We examined other kinds of sodium phosphate compounds as additives. Table II shows results of other additives, Na_2HPO_4 and $\text{Na}_4\text{P}_2\text{O}_7$, in storage performance. The storage performances are improved to reach 75 and 66% for 5% Na_2HPO_4 and $\text{Na}_4\text{P}_2\text{O}_7$, respectively, which are better than that for 5% of Na_3PO_4 . The result is partly explained as follows. Bases would generally suppress the acid hydrolysis of PF_6^- ion to hydrofluoric acid (HF) and then lower the dissolution of Mn ions out of LiMn_2O_4 . However, strong bases could cause some damage to LiMn_2O_4 while weak bases do not. The solubility of a Mn compound itself is another important factor. As the Mn phosphate salts' solubilities are low in aqueous solutions, it is low in the electrolyte solution. Therefore, Mn ions have little influence on the anode. $\text{Na}_4\text{P}_2\text{O}_7$ as a drying agent may also suppress the hydrolysis of PF_6^- . The improvement has been explained from the above reasons, but the detail mechanism of the improvement has remained unclear.

Figure 2 shows the results of the cycle-performance tests for the case including these additives. The additives of 5 and 10% Na_2HPO_4 give 73 and 58% of capacity retentions, respectively, at the 100th cycle, and 5 and 10% of $\text{Na}_4\text{P}_2\text{O}_7$ addition result in 70 and 64% of retentions, respectively. In Fig. 2, smoother decreasing is

Table II. Storage and cycle performances of $\text{Li}_{1.04}\text{Mn}_{1.96}\text{O}_4/\text{graphite}$ cells at the 100th cycle at 55°C . Na_2HPO_4 or $\text{Na}_4\text{P}_2\text{O}_7$ is used as an additive. The electrolyte is 1 M $\text{LiPF}_6/\text{EC}:\text{DMC}$ (1:2).

| Additives | 5% Na_2HPO_4 | 10% Na_2HPO_4 | 5% $\text{Na}_4\text{P}_2\text{O}_7$ | 10% $\text{Na}_4\text{P}_2\text{O}_7$ |
|------------------------|------------------------------|-------------------------------|--------------------------------------|---------------------------------------|
| Storage performance | | | | |
| Capacity retention (%) | 75 | 71 | 66 | 79 |
| Mn dissolution (%) | 0.005 | 0.002 | 0.049 | 0.018 |
| Cycle performance | | | | |
| Capacity retention (%) | 73 | 58 | 70 | 64 |

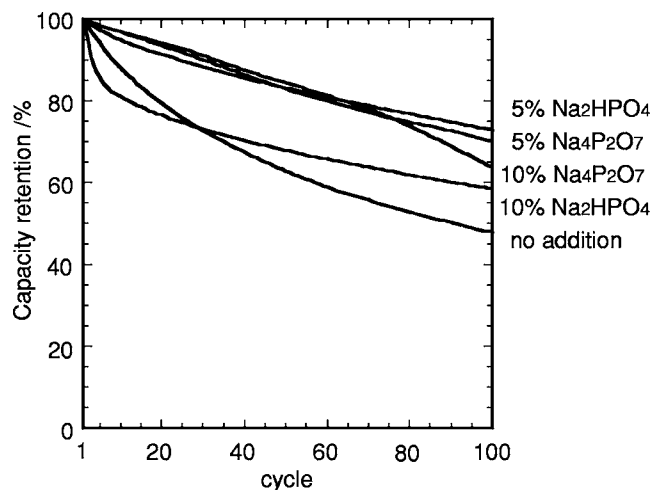
**Figure 2.** Cycle performance for $\text{Li}_{1.04}\text{Mn}_{1.96}\text{O}_4/\text{graphite}$ cells with Na_2HPO_4 or $\text{Na}_4\text{P}_2\text{O}_7$ as an additive at 55°C . The electrolyte is 1 M $\text{LiPF}_6/\text{EC}:\text{DMC}$ (1:2).

Table III. Storage and cycle performances of $\text{Li}_{1.04}\text{Mn}_{1.96}\text{O}_4$ /graphite cells at the 100th cycle at 55°C in the various 1 M electrolytes/EC:DMC (1:2).

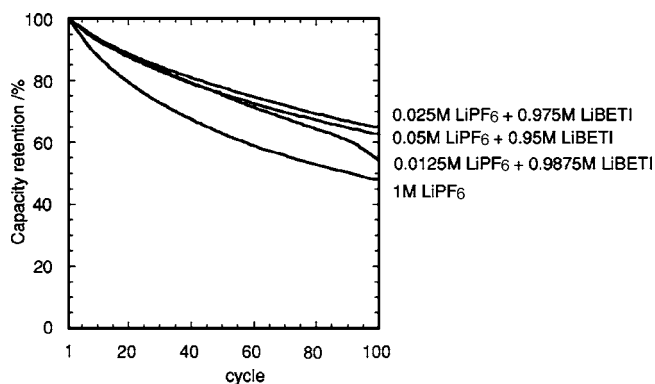
| Electrolyte | 1 M LiPF_6 | 0.05 M LiPF_6 0.95 M LiBETI | 0.025 M LiPF_6 0.975 M LiBETI | 0.0125 M LiPF_6 0.9875 M LiBETI |
|------------------------|---------------------|---|---|---|
| Storage performance | | | | |
| Capacity retention (%) | 47 | 77 | 74 | 84 |
| Mn dissolution (%) | 0.28 | 0.32 | 0.51 | 0.69 |
| Cycle performance | | | | |
| Capacity retention (%) | 48 | 63 | 65 | 54 |
| Mn dissolution (%) | 0.78 | 1.84 | 2.32 | 2.71 |

observed in the capacity retention curves for 5% Na_2HPO_4 and $\text{Na}_4\text{P}_2\text{O}_7$. However, these capacity retentions are not considered practically sufficient.

The effect of substituting the LiPF_6 electrolyte for another is also examined. The PF_6^- anions in LiPF_6 are easily hydrolyzed to produce HF, which dissolves LiMn_2O_4 to generate Mn ions. As a result, their Mn ions would react with solid electrolyte interface (SEI) on the negative electrode surface, and it would lead to capacity loss. When a polyatomic anion of a Li compound is hardly hydrolyzed when used as an electrolyte instead of LiPF_6 , the capacity of the cell with LiMn_2O_4 is expected to keep more constant even at a higher temperature because of less deposition of Mn ions on the negative electrode. For such a purpose, we choose LiBETI as an electrolyte compound. However, in the use of 100% LiBETI, cells are hard to cycle because materials used in the cell may corrode electrochemically. Then the mixed electrolytes of LiBETI and LiPF_6 are used at the ratios of 0.9875:0.0125 M, 0.975:0.025 M, and 0.95:0.05 M, respectively, in the 1:2 solvent mixture of EC/DMC.

Table III shows the results of storage performance for the cell with $\text{Li}_{1.04}\text{Mn}_{1.96}\text{O}_4$ and the graphite without any additives at 55°C. The storage performances are improved up to 77, 74, and 84% for 0.05 M LiPF_6 + 0.95 M LiBETI, 0.025 M LiPF_6 + 0.975 M LiBETI and 0.0125 M LiPF_6 + 0.9875 M LiBETI, respectively, in contrast to 47% for 1 M LiPF_6 . But, Mn dissolution increases to 0.32, 0.51, and 0.69% from 0.28% along with the decrease of the concentration of LiPF_6 .

Figure 3 shows the typical results of cycle performances for the cells using LiBETI as an electrolyte. The electrolytes of 0.05 M LiPF_6 + 0.95 M LiBETI and 0.025 M LiPF_6 + 0.975 M LiBETI results in 63 and 65% of good cycle retention, respectively, at the 100th cycle. In the mixture of 0.0125 M LiPF_6 + 0.9875 M LiBETI, the result is as low as 54%. However, it is better than that for 1 M LiPF_6 without LiBETI. The capacity reten-

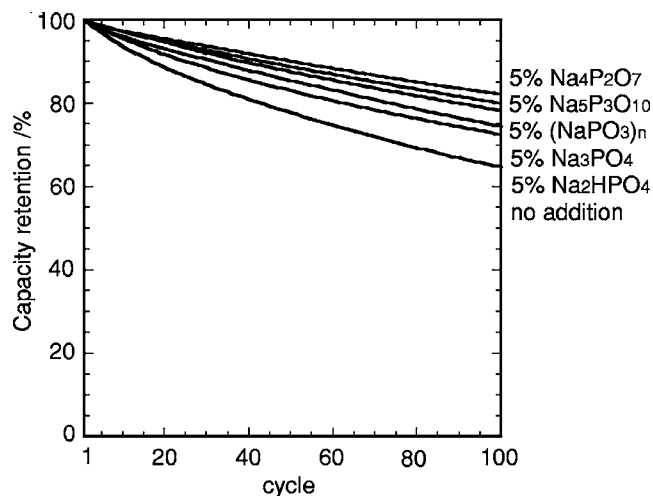
**Figure 3.** Cycle performance of $\text{Li}_{1.04}\text{Mn}_{1.96}\text{O}_4$ /graphite cells at 55°C. The electrolytes are 1 M LiPF_6 , 0.95 M LiBETI + 0.05 M LiPF_6 , 0.975 M LiBETI + 0.025 M LiPF_6 , and 0.9875 M LiBETI + 0.0125 M LiPF_6 /EC:DMC (1:2).

tion curves show smooth and gradual decay for 0.95 or 0.975 M of LiBETI, but that for 0.0125 M LiPF_6 + 0.9875 M LiBETI rapidly decreases at the cycles after about 80 cycles in each test. The optimum electrolyte condition as to the cycle performance is obtained for the mixture of 0.025 M LiPF_6 + 0.975 M LiBETI.

On the basis of the above results, the cycle performance was tested for the case of the optimum combination of the addition of 5% of various compounds of phosphate and the use of the mixed electrolyte, 0.025 M LiPF_6 + 0.975 M LiBETI. Table IV and Fig. 4 show the results at the 100th cycle at 55°C. Figure 4 demonstrates all curves are smooth with no irregular fluctuations. The capacity retention is more than 80% for $\text{Na}_4\text{P}_2\text{O}_7$ and $\text{Na}_5\text{P}_3\text{O}_{10}$, which is a sufficiently practical level. The present study gives some important and interesting points in clarification of the mechanism of the deterioration and improvement of capacity fading. It is left ambiguous why the addition of sodium phosphate compounds are so effective in decreasing capacity loss in the case of the LiBETI + LiPF_6 electrolyte mixture in spite of the increase of Mn deposition on the negative electrode.

Table IV. Cycle performances of $\text{Li}_{1.04}\text{Mn}_{1.96}\text{O}_4$ /graphite cells at the 100th cycle with various phosphate additives at 55°C. The electrolyte is 0.975 M LiBETI + 0.025 M LiPF_6 /EC:DMC (1:2).

| Additives | No additives | Na_3PO_4 | Na_2HPO_4 | $\text{Na}_4\text{P}_2\text{O}_7$ | $\text{Na}_5\text{P}_3\text{O}_{10}$ | $(\text{NaPO}_3)_n$ |
|------------------------|--------------|--------------------------|---------------------------|-----------------------------------|--------------------------------------|---------------------|
| Capacity retention (%) | 65 | 74 | 73 | 82 | 80 | 78 |

**Figure 4.** Cycle performance of $\text{Li}_{1.04}\text{Mn}_{1.96}\text{O}_4$ /graphite cells with various phosphate additives at 55°C. The electrolyte is 0.975 M LiBETI + 0.025 M LiPF_6 /EC:DMC (1:2).

Conclusion

In $\text{Li}_{1.04}\text{Mn}_{1.96}\text{O}_4/\text{graphite}/\text{cells}$, some sodium phosphate additives and the mixed electrolyte of LiBETI and LiPF_6 were examined to aim at improving their cells' cycle performance at 55°C . The 5% Na_2HPO_4 and $\text{Na}_4\text{P}_2\text{O}_7$ additives give 73 and 70% of the cycle performances at the 100th cycle, respectively, and the optimum electrolyte mixture is that of 0.025 M LiPF_6 and 0.975 M LiBETI for the best cycle performance. The best capacity retention is more than 80% in the case of 5% $\text{Na}_4\text{P}_2\text{O}_7$ or $\text{Na}_5\text{P}_3\text{O}_{10}$ additive in combination with such electrolyte solution. This value of capacity retention is considered to be a sufficient level for the practical use.

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