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Thermal Reactions Between Delithiated Lithium Nickelate and Electrolyte Solutions

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Lithium nickelate is a promising electrode material for lithium-ion batteries, however, its low thermal stability is a problem that should be solved. We studied the thermal stability of delithiated lithium nickelate compounds in the presence of electrolyte solvents/solutions. We measured the exothermal heat generation of the reaction system using differential scanning calorimetry. We examined simple systems such as ethylene carbonate with $Li_{0.2}NiO_2$, using hermetically sealed pans that allowed us to perform the experiments under constant mass conditions. The data were quantitatively analyzed to propose possible reaction mechanisms for the exothermal behavior. We attributed the main source of the exothermal heat to organic solvent combustion caused by oxygen released from the nickelate. We studied similar reactions using other solvents/solutions and electrochemically or chemically delithiated nickelate samples. We also examined the behavior of lithium cobaltate for comparison. We discuss the effect of partial substitution for nickel on thermal stability.

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Lithium nickelate is an attractive positive electrode material for lithium-ion batteries because of its comparatively low cost and large capacity.[1-3] However, its stability must be improved to meet safety standards, because highly delithiated compounds Li_xNiO_2 ($x \leqq 0.3$) decompose exothermally at around 200°C.[4-6] It has recently been reported that there is even greater exothermal heat generation when the nickelate material is heated in the presence of organic electrolyte solutions.[7-15] However, the origin of this large heat generation has remained unclear because of the complexity of the reaction system, which contains many components such as electrode material, electrolyte solute, and mixed organic solvents. For examining such thermal behavior, differential scanning calorimetry (DSC) has been widely used.[5-17] As DSC shows the amount of generated heat quantitatively, a study of simple reaction systems, for example, oxide with a single solvent, may be the key to discovering the reaction mechanism.

In this study we report the thermal behavior of Li_xNiO_2 in contact with electrolyte solutions using DSC coupled with thermogravimetry (TG). We examined reactions involving ethylene carbonate (EC) in particular detail, because EC is often used as the main component in electrolyte solutions. We tested both electrochemically and chemically delithiated compounds and compared their behavior with that of lithium cobaltate. We also discuss the effect of partial substitution for nickel on the thermal stability of the delithiated material.

Experimental

We prepared nearly stoichiometric $LiNiO_2$ samples by heating a mixture of $LiOH \cdot H_2O$, $LiNO_3$, and $Ni(OH)_2$ (1:1:1 in molar ratios) in air at 500°C for 6 h and then at 700°C for 24 h. We removed unreacted lithium compounds by washing the heated product with distilled water. The structural and electrochemical characteristics of this compound are detailed elsewhere.[18] We used $LiCoO_2$ powder (Nippon Chemical Industrial) as received. All the electrolyte solutions and organic solvents were of battery grade (Tomiyama Pure Chemical Industries) and contained less than 20 ppm of water.

The electrochemical cell we used contained a metallic lithium counter electrode and a 1 mol dm^{-3} $LiPF_6$ electrolyte solution in equal volumes of EC and dimethyl carbonate (DMC). The working electrode mixture consisted of the oxide material (70 wt %), acetylene black (AB, 25 wt %), and polytetrafluoroethylene (PTFE, 5 wt %). We prepared electrochemically delithiated compounds by charging the cell at 0.1 mA cm^{-2}. We estimated the lithium content of the delithiated compounds (x in Li_xNiO_2 or Li_xCoO_2) using the transferred charge and the weight of the electrode. For example, when a charge of 220 mAh (g-oxide)$^{-1}$ passed for an $LiNiO_2$ electrode (275 mAh g^{-1} for one-electron reaction), we expected the product to be $Li_{0.2}NiO_2$. We sampled an electrode with a nominal composition of $Li_{0.2}NiO_2$ and conducted the chemical analysis using inductively coupled plasma emission (ICPE) spectroscopy. The analysis indicated that the Li/Ni ratio was 0.23 ± 0.03, suggesting that our estimation was valid within the margin of experimental error. After the charging process was stopped at desired values, we allowed the electrodes to relax for 1 week in the cell and then removed them. We washed the electrodes with DMC, and then dried them in a vacuum at room temperature.

We prepared chemically delithiated samples as follows. We added the $LiNiO_2$ sample to a 0.6 mol dm^{-3} aqueous solution of sulfuric acid. The initial molar ratio of $H^+/LiNiO_2$ was 5. We stirred the mixture at 25°C for 5 h and then filtered the product. We washed the filtrate powder with acetone to remove the water on the surface and then dried it in a vacuum at room temperature. The sample had a chemical composition of $Li_{0.1}NiO_2$, as determined by ICPE analysis, and was electrochemically active.[6]

We measured the DSC-TG behavior (Rigaku TAS-100) in an argon atmosphere at a heating rate of 10°C min^{-1}. For measuring the amount of heat based on reactant weights, it was necessary to use hermetically sealed (HS) stainless steel pans to prevent solvent volatilization. We were able to perform the experiments under constant mass conditions up to 400°C, with a mixture of a few milligrams of the delithiated sample and electrolyte solvent/solution. We occasionally used crimp sealed (CS) aluminum pans to test the reaction under more practical pressure conditions. The HS and CS pans can withstand internal pressures of 50 and 3 atm, respectively. The use of the CS pans allowed us to characterize the structure of the product after DSC-TG measurement, using X-ray diffraction (XRD), (Rigaku RU-200, RAD-rX) with Cu Kα radiation. We analyzed the water evolution from the reaction system using the Karl-Fischer method (Mitsubishi Chemicals CA-06). We placed the sample on a heating boat in a closed tube in which there was a dry argon gas flow. The argon gas carried the water that evaporated from the sample to a water detector.

Results and Discussion

Reactions between electrochemically obtained Li_xNiO_2 and EC.—Figure 1 shows the DSC behavior of EC and electrochemically obtained $Li_{0.2}NiO_2$ that we tested in HS pans. When we heated only EC, we observed endothermal heat generation at 270-330°C,

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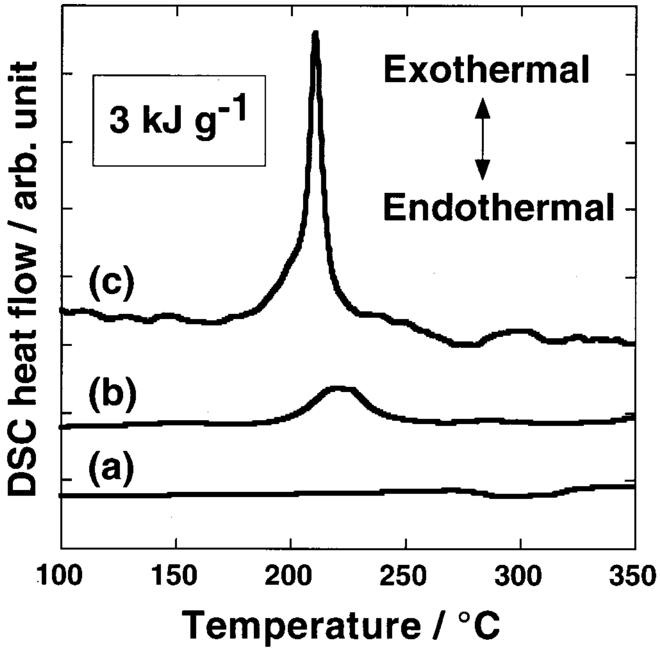

Figure 1. DSC behavior of EC and electrochemically obtained $Li_{0.2}NiO_2$ tested in HS pans: (a) EC alone, (b) $Li_{0.2}NiO_2$ alone, and (c) EC and $Li_{0.2}NiO_2$ (1:1 in weight ratio). The inset in the figure shows a benchmark for the amount of heat.

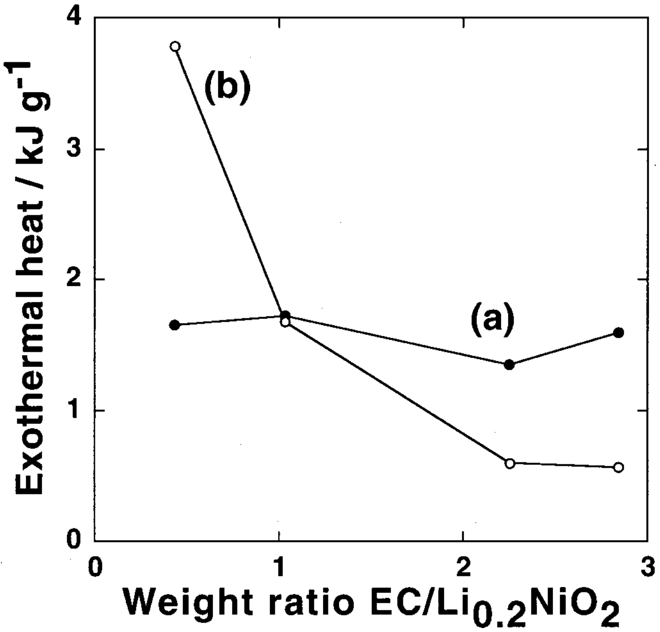

Figure 2. Observed amount of heat based on (a) $Li_{0.2}NiO_2$ or (b) EC weight for different EC/$Li_{0.2}NiO_2$ ratios.

which we ascribed to EC vaporization under the HS conditions. The $Li_{0.2}NiO_2$ electrode mixture, containing AB and PTFE, had a small exothermal peak at 170-230°C. When we mixed these two components of approximately equal weights and heated them, much more exothermal heat was generated than with nickelate alone.

To clarify the origin of the heat generation, we measured the amount of exothermal heat with various reactant weight ratios of EC/$Li_{0.2}NiO_2$. An exothermal peak, similar to that in Fig. 1c, was observed in all the DSC profiles. The amount of the exothermal heat (at 170-230°C) was nearly proportional to the nickelate weight rather than the EC weight, as shown in Fig. 2, and the value was about 1.6 kJ (g-oxide)$^{-1}$. This suggests that the large heat generation shown in Fig. 1c chiefly originates from nickelate-related reactions, which then induces reactions involving EC. It is therefore important to understand how the nickelate alone decomposes. According to previous reports,[1,4,5] the decomposition follows Reaction 1, resulting in the formation of a more stable nickelate phase with a rock-salt structure and oxygen

$$Li_xNiO_2 \rightarrow (1 + x)Li_{x/(1+x)}Ni_{1/(1+x)}O + (1 - x)/2\ O_2 \quad [1]$$

Based on this nature of nickelate, there are two possible reactions that could cause a large amount of heat to be generated in the presence of EC. Reaction 2 is the catalytic decomposition of EC to form carbon dioxide and ethylene oxide,[19] which could be initiated by the exothermal heat arising from Reaction 1. Reaction 3 is EC combustion, where the oxygen from the nickelate could oxidize EC to form carbon dioxide and water

$$C_3H_4O_3 \rightarrow CO_2 + C_2H_4O \quad [2]$$

$$C_3H_4O_3 + \frac{5}{2}O_2 \rightarrow 3CO_2 + 2H_2O \quad [3]$$

Carbon dioxide is commonly observed as a reaction (particularly oxidation) product of organic solvents[20-22] and could be observed in both Reactions 2 and 3. We examined possible water production using the Karl-Fischer method. The reaction boat was kept at a fixed temperature of 200°C, where the exothermal reaction certainly occurs (see Fig. 1c) and we can minimize the EC evaporation that occurs above 170°C (see below). While water was hardly detected on heating EC alone, we detected a considerable amount of water when we heated the mixture of EC and $Li_{0.2}NiO_2$, suggesting that EC mainly decomposes in accordance with Reaction 3.

Reaction 3 seems plausible also because the reaction heat was proportional to the nickelate weight. We calculated the expected amount of heat based on Reaction 3 and compared it with the experimentally observed value to confirm the validity of this suggestion. Reaction 1 indicates that when we heat 1 g $Li_{0.2}NiO_2$, 0.14 g oxygen evolves. This amount of oxygen can burn 0.15 g of EC, according to Reaction 3. The EC combustion heat is reported to be 13 kJ (g-EC)$^{-1}$.[23] Consequently, 1 g $Li_{0.2}NiO_2$ generates a heat of 2.0 kJ. This amount, 2.0 kJ (g-oxide)$^{-1}$, is close to the value that we observed in the DSC measurements (see Fig. 2), supporting the idea that Reaction 3 is appropriate.

There are several possible explainations for the difference between the expected and experimental values. The experimental data contain heat caused by the self-decomposition of the oxide (exothermal), oxygen vaporization (endothermal), and EC vaporization (endothermal). We used data on combustion heat in the standard thermodynamic state (1 atm, 25°C), which were the only data available. However, they may be invalid at 200°C under HS conditions. There would be a smaller amount of oxygen at around 200°C than expected by Reaction 1, because the oxygen evolves at temperatures higher than 190°C up to 500°C.[6] EC would be directly oxidized by the delithiated nickelate (Reaction 4), rather than by the released oxygen (Reaction 3)

$$25Li_xNiO_2 + 4C_3H_4O_3 \rightarrow 30Li_{1/6}Ni_{5/6}O + 12CO_2 + 8H_2O \quad [4]$$

Nevertheless, we concluded that the exothermal heat generation can be attributed mainly to Reactions 1 and 3 because they can satisfactorily account for the observed data.

Nickel compounds are generally catalytic and their surfaces known to be active with regard to electrolyte decomposition.[21,24] Accordingly, Reaction 3 may also be catalyzed in the presence of the nickelate surface. In fact, nickelate surface modification is partly effective in suppressing the exothermal heat generation.[13] However,

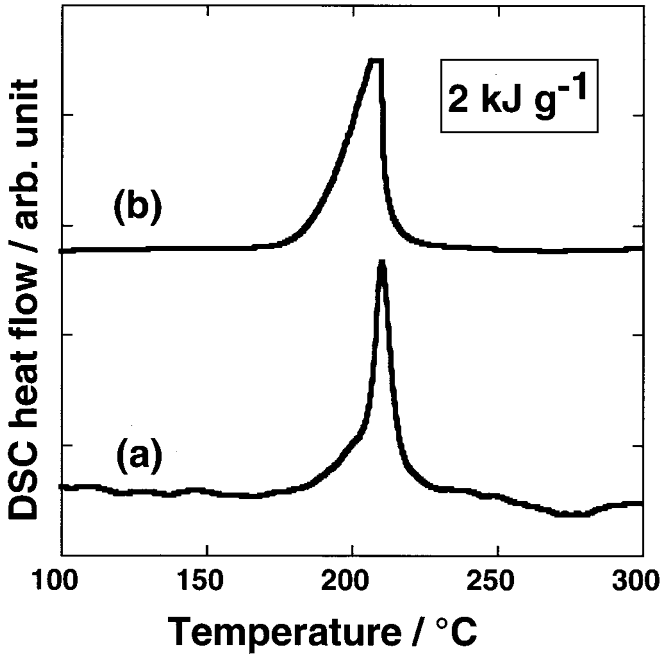

Figure 3. DSC behavior of EC with (a) electrochemically delithiated $Li_{0.2}NiO_2$ and (b) chemically delithiated $Li_{0.1}NiO_2$.

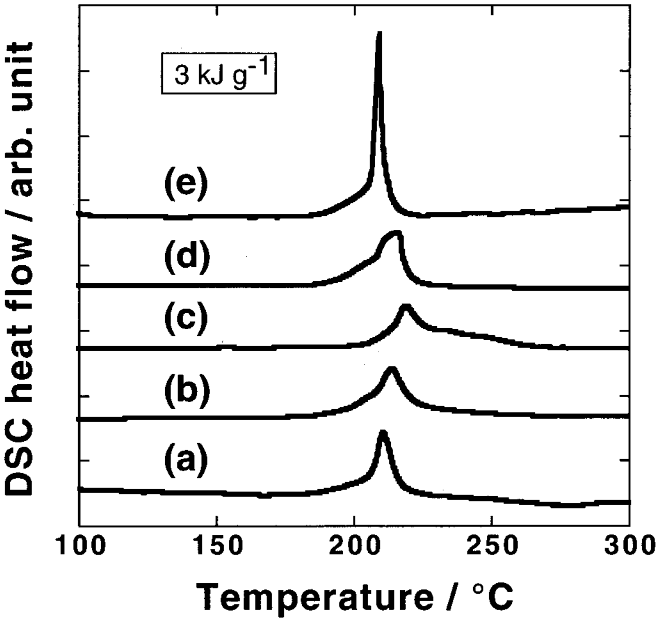

Figure 4. DSC behavior of $Li_{0.2}NiO_2$ with (a) EC, (b) PC, (c) gBL, (d) DEC, and (e) DMC (see Table I for abbreviations).

there was no exothermal reaction when we heated EC with NiO or $LiNiO_2$. We therefore believe that oxygen released from the nickelate is principally responsible for the large exothermal heat generation shown in Fig. 1c.

Reactions between chemically obtained Li_xNiO_2 and EC.—We subsequently observed the thermal behavior of chemically delithiated $Li_{0.1}NiO_2$ and EC using the HS pan. This allowed us to clarify how conductive agent (AB) and binder (PTFE) contribute to the reaction. The DSC behavior was similar to that of electrochemically delithiated $Li_{0.2}NiO_2$, as shown in Fig. 3. The exothermal heat of 1.8 kJ $(\text{g-oxide})^{-1}$ was again close to the expected value of 2.3 kJ $(\text{g-oxide})^{-1}$, which we calculated from Reactions 1 and 3 with $x = 0.1$. We therefore concluded that these electrode additives have essentially no effect on the exothermal behavior at around 200°C.

Reactions of various solvents and solutions.—We examined the thermal behavior of other organic solvents with electrochemically delithiated $Li_{0.2}NiO_2$ using the HS pan. Figure 4 shows the DSC behavior. Although the peak shapes are somewhat different from each other, the exothermal peak appeared at around 200°C regardless of the solvent used, suggesting that the reactions originated from the nickelate decomposition reaction. Table I summarizes the amount of generated heat, which was close to that expected for the corresponding solvent combustion. Although we have no data available for propylene carbonate (PC) combustion, the observed value seems reasonable because PC is structurally similar to EC. It is noteworthy that the amount of heat is nearly 2 kJ $(\text{g-}Li_{0.2}NiO_2)^{-1}$ for all the cases we studied. In general, organic compounds consisting of many carbon/hydrogen atoms (hence having a large molecular weight) exhibit large combustion heat but require a large amount of oxygen for combustion. In this study the available amount of oxygen was limited by Reaction 1; accordingly, the heat produced was almost the same regardless of the solvent.

To clarify the influence of the electrolyte solute $LiPF_6$ on the thermal properties, we measured the DSC behavior of a 1 mol dm^{-3} $LiPF_6$ solution in equal volumes of EC and DMC with and without $Li_{0.2}NiO_2$. We set the nickelate-to-solution weight ratio at unity. As shown in Fig. 5, there was an exothermal peak at around 280°C in both cases. This can be attributed to the reaction of $LiPF_6$ (or its decomposition product such as PF_5) with gaseous EC, because EC evaporation occurs in the HS pan at this temperature (see Fig. 1a). A similar result has recently been reported.[17] A large exothermal peak at 210°C in Fig. 5b can be attributed to the combustion of the organic solvent because the phenomenon is similar to that in Fig. 1c. There was additional heat at around 250°C in the presence of both $Li_{0.2}NiO_2$ and $LiPF_6$; nevertheless, the combustion of the organic solvent that occurs at a lower temperature is more important in terms of battery safety.

Reactions under ambient pressure using CS pans.—Figure 6 shows the thermal behavior of the electrochemically delithiated $Li_{0.2}NiO_2$ with EC that we tested in the HS and CS pans. While the weight remained unchanged with the HS pan at temperatures up to 400°C, there was a weight loss with the CS pan at temperatures above 170°C (see TG behavior shown in the figure), indicating that the EC vaporization occurred before the exothermal heat was generated. However, the amount of heat was similar to that observed with the HS pans, as shown. When we tested the reaction between $Li_{0.2}NiO_2$ and DMC in the CS pan, we observed much less exothermal heat. This was because there was no DMC left in the pan at 200°C, as deduced from the TG data, and we actually observed the thermal behavior of $Li_{0.2}NiO_2$ alone, like that shown in Fig. 1b. These results suggest that EC with a high boiling point (248°C at an ambient pressure) can remain in the battery at the nickelate decomposition temperature, even if the battery is equipped with a safety vent. Accordingly, reactions involving EC are important in terms of battery safety.

We analyzed the XRD pattern of solid residues after the DSC-TG measurement when we used the CS pans. The residue after heating $Li_{0.2}NiO_2$ with EC up to 400°C was mostly $Li_{1-z}Ni_zO$ ($z \approx 5/6$) with a rock salt structure,[28] as expected. However, when we used a relatively small amount of EC compared with the nickelate (typically $EC/Li_{0.2}NiO_2 \ll 1$ in the weight ratio), there was a by-product of metallic nickel (Ni) together with the $Li_{1-z}Ni_zO$ phase. Figure 7b shows the XRD pattern of the residue for $EC/Li_{0.2}NiO_2 = 0.5$, demonstrating a few peaks corresponding to Ni. Using the intensities of these peaks, we estimated the weight ratio in the product to be $Li_{1-z}Ni_zO:Ni = 9:1$. Figure 8 provides the corresponding DSC curves. The observed amount of heat was around 1.8 kJ

Table I. Expected and observed amounts of heat for reactions between $Li_{0.2}NiO_2$ and organic solvents.

Solvent	Heat of combustion /kJ (g-solvent)$^{-1}$	Moles of O_2 used for combustion	Expected heat /kJ (g-$Li_{0.2}NiO_2$)$^{-1}$	Observed heat /kJ (g-$Li_{0.2}NiO_2$)$^{-1}$
Ethylene carbonate (EC)	13 (Ref. 23)	2.5	2.0	1.6
Propylene carbonate (PC)	(Not available)	4	-	2.0
γ-Butyrolactone (gBL)	22 (Ref. 25)	4.5	1.8	1.9
Diethyl carbonate (DEC)	21 (Ref. 26)	6	1.8	2.0
Dimethyl carbonate (DMC)	16 (Ref. 27)	3	2.1	2.1

(g-$Li_{0.2}NiO_2$)$^{-1}$ in both cases, showing that Ni formation has only a minor effect on the overall reaction mechanism. Nevertheless, when EC/$Li_{0.2}NiO_2$ = 0.5, the DSC peak was very sharp as shown in Fig. 8b, and this phenomenon probably corresponds to the Ni formation. The detailed mechanism for this Ni formation is unclear at the moment. A possible explanation is that when the EC/$Li_{0.2}NiO_2$ ratio is small, the nickelate-catalyzed reaction (Reaction 2) proceeds and unstable (explosive) ethylene oxide is formed as an intermediate species, which then reduces the nickelate to Ni. This hypothesis certainly requires further study. As we never observed the formation of Ni when we heated Li_xNiO_2 alone, it is at least clear that Ni formation requires a reducing agent such as EC.

It has been reported that Li_xNiO_2 turns into $Li_{1-z}Ni_zO$ via an intermediate phase with a spinel-related structure.[1,4,29] To observe the effect of this spinel phase formation, we measured the DSC behavior of $Li_{0.2}NiO_2$ and EC using CS pans and interrupted the measurement at different temperatures. However, the products were either $Li_{-z}Ni_zO$ or remaining reactants, and no spinel-related phase was seen. This is probably because, in the presence of reducing agents, $Li_{1-z}Ni_zO$ is more stable than the spinel-related phase.

Stability of Li_xNiO_2 and Li_xCoO_2.—We examined the thermal behavior of EC with delithiated lithium cobaltate comparatively. $Li_{0.5}CoO_2$ was prepared by charging the $LiCoO_2$ electrode. When we heated the mixture of $Li_{0.5}CoO_2$ and EC in the HS pan, there was exothermal heat of 0.9 kJ (g-oxide)$^{-1}$ with a heat peak at 250°C, as shown in Fig. 9. $Li_{0.5}CoO_2$ is known to decompose in accordance with Reaction 5,[4] leading to 0.06 g of oxygen being released from 1 g $Li_{0.5}CoO_2$. This value provides the expected amount of combustion heat of 0.8 kJ (g-oxide)$^{-1}$, which again nearly accords with the experimental data

$$Li_{0.5}CoO_2 \rightarrow \frac{1}{2}LiCoO_2 + \frac{1}{6}Co_3O_4 + \frac{1}{6}O_2 \qquad [5]$$

Recent work using accelerating rate calorimetry has also shown that solvent combustion occurs with oxygen released from Li_xCoO_2[30] and also from $Li_xMn_2O_4$.[31]

Figure 10 shows the voltage-lithium concentration profiles of Li_xNiO_2 and Li_xCoO_2 electrodes during delithiation at a constant current density of 0.1 mA cm^{-2}. As shown, $Li_{0.2}NiO_2$ and $Li_{0.5}CoO_2$ were obtained at almost the same potential of 4.2 V *vs.* Li/Li$^+$. Nevertheless, considerably more heat was generated for the former than the latter. This is because the nickelate is readily delithiated and reaches high oxidation states, resulting in more oxygen generation on heating than with the cobaltate. Moreover, when we adopt $x = 0.5$ in Reaction 1, we obtain the following

$$Li_{0.5}NiO_2 \rightarrow \frac{3}{2}Li_{1/3}Ni_{2/3}O + \frac{1}{4}O_2 \qquad [6]$$

Reactions 5 and 6 show that even if the same amount (50%) of lithium is extracted, the cobaltate produces less oxygen, and hence, less combustion heat, than the nickelate. Figure 9 shows another important feature of the cobaltate, namely, that it has a higher reac-

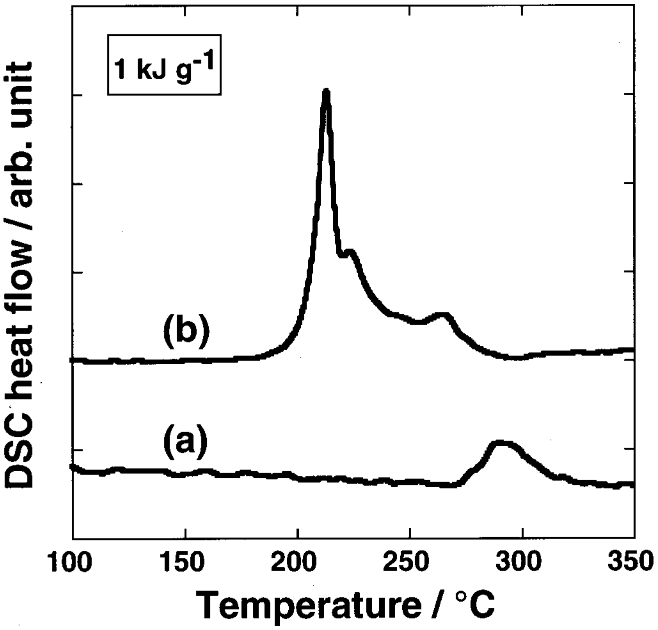

Figure 5. DSC behavior of 1 mol dm^{-3} $LiPF_6$ solution in DMC + EC (1:1) (a) without and (b) with $Li_{0.2}NiO_2$.

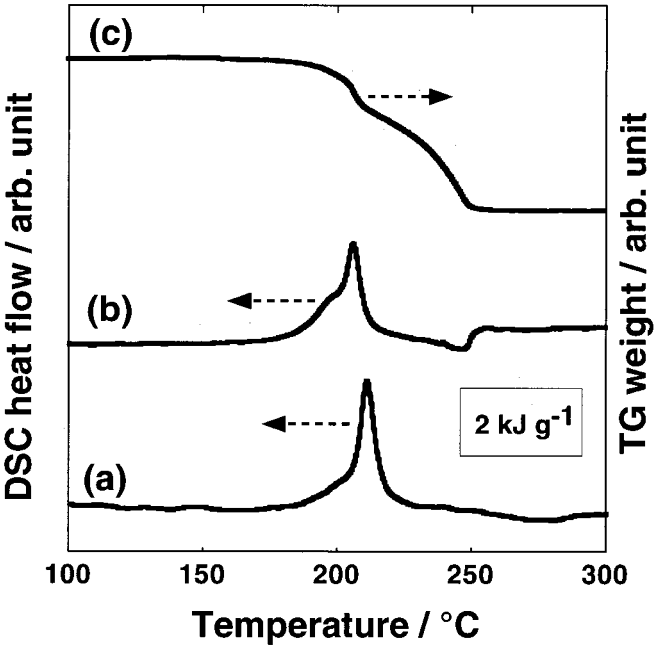

Figure 6. Thermal behavior of EC and $Li_{0.2}NiO_2$: (a) DSC behavior for the HS pan; (b) DSC and (c) TG behavior for the CS pan.

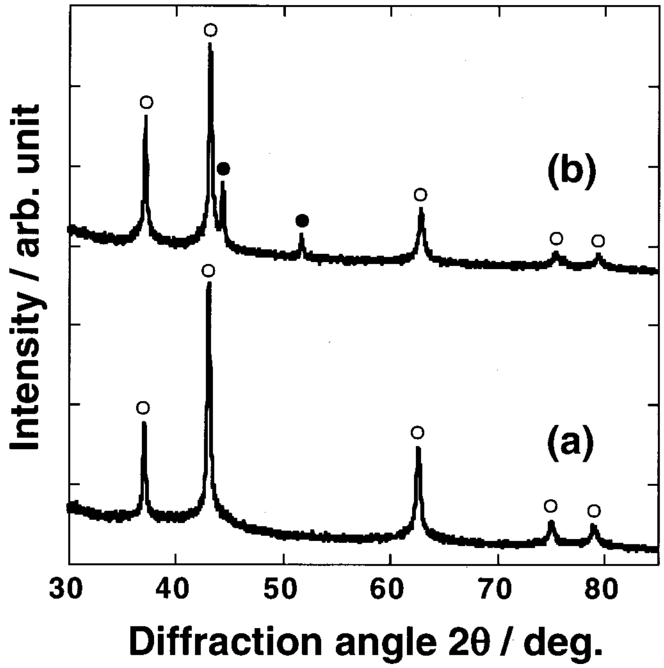

Figure 7. XRD patterns of residues for EC/$Li_{0.2}NiO_2$ = (a) 1.0 and (b) 0.5: (○) $Li_{1/6}Ni_{5/6}O$ and (●) metallic nickel peaks.

tion temperature than the nickelate. This temperature is as high as the boiling point of EC. In fact, when we heated the cobaltate and EC using the CS pan, we observed no EC combustion heat but only a small amount of exothermal heat caused by Reaction 5. This suggests that it is possible to avoid the EC combustion caused by the $Li_{0.5}CoO_2$ decomposition if the battery has a safety vent allowing the release of gaseous EC. These characteristics account for the insufficient safety of nickelate electrodes when compared with cobaltate electrodes.[4,5,8,9]

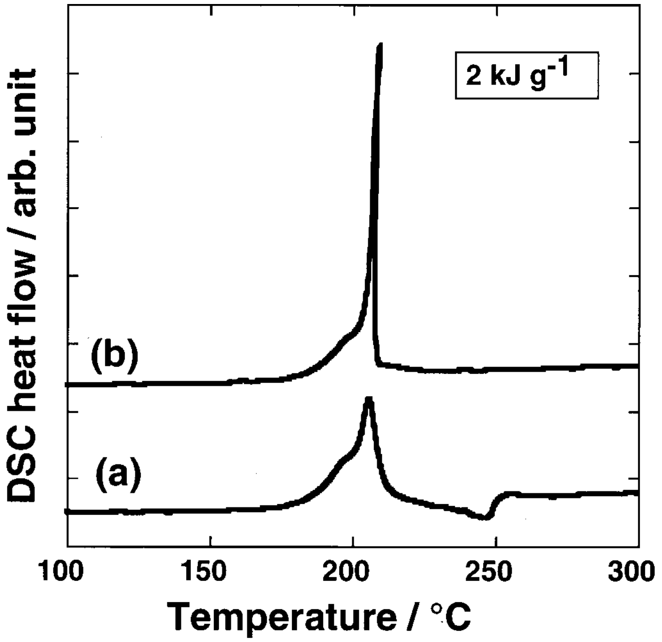

Figure 8. DSC behavior for (a) EC/$Li_{0.2}NiO_2$ = 1 and (b) EC/$Li_{0.2}NiO_2$ = 0.5 in the CS pans.

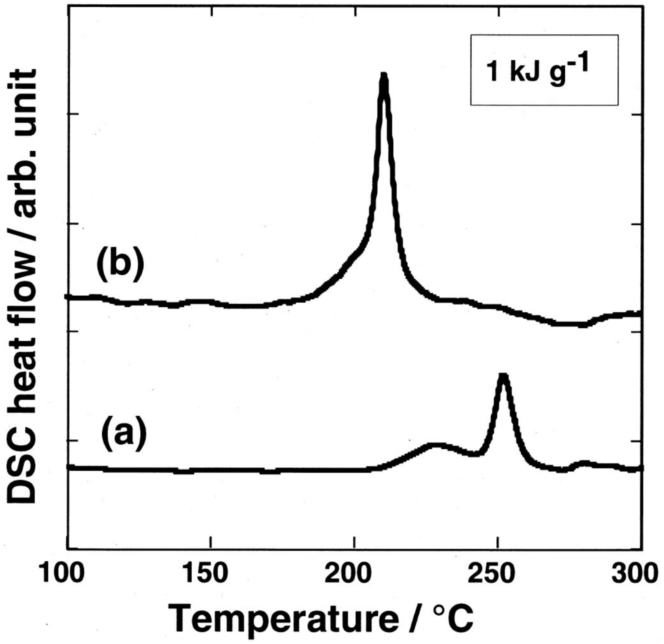

Figure 9. DSC behavior of EC with (a) $Li_{0.5}CoO_2$ and (b) $Li_{0.2}NiO_2$ in the HS pans.

It is thus desirable to improve the insufficient thermal stability of Li_xNiO_2. Partial substitution for nickel seems to be a promising approach, as several research groups have proposed useful substituents such as aluminum,[7] cobalt,[14] aluminum-cobalt,[10,15] cobalt-manganese,[12] magnesium-titanium,[9] and others.[32] Of these, cobalt substitution has been well studied because the cobaltate is clearly more stable than the nickelate as discussed previously. We have recently shown that manganese or titanium-substituted lithium nickelate exhibits endothermal behavior when dilithiated and heated without electrolyte solutions.[33,34] In our preliminary experiments these compounds unfortunately exhibited exothermal behavior when heated with electrolyte solutions, however, some had a smaller exo-

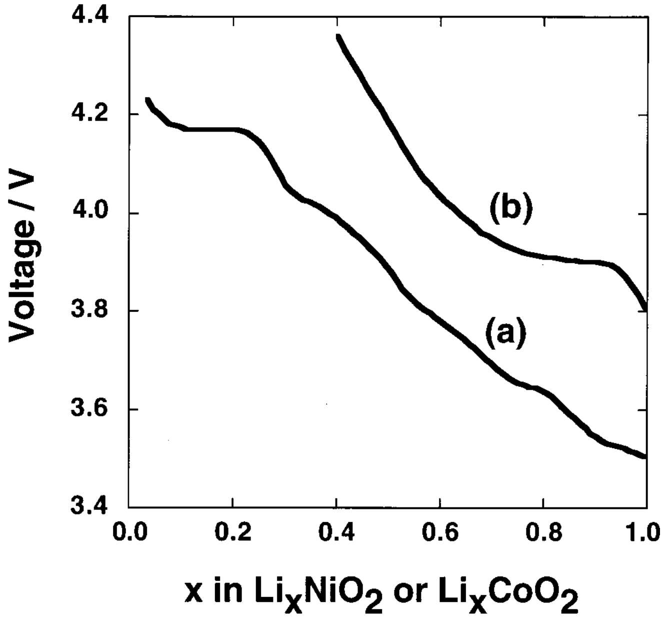

Figure 10. Profiles of (a) Li_xNiO_2 and (b) Li_xCoO_2 electrodes during delithiation at a constant current density of 0.1 mA cm^{-2}.

thermal peak with a higher reaction temperature than the nonsubstituted nickelate. We are currently unable to explain the effect of these substituents; nevertheless, we believe it is important to select substituents that can suppress solvent combustion.

Conclusions

Delithiated lithium nickelate generates a large amount of exothermal heat when heated with organic electrolyte. We attributed the main origin of the heat to the organic solvent combustion caused by oxygen released from the nickelate, while the electrolyte solute $LiPF_6$ has a minor effect on the thermal behavior. The amount of heat is largely independent of the solvent because the amount of released oxygen is governed by the amount of nickelate. Reactions involving EC are of particular importance with regard to battery safety due to its high boiling point. Li_xNiO_2 is reduced to $Li_{x/(1+x)}Ni_{1/(1+x)}O$ and occasionally also to metallic nickel. Solvent combustion also occurs when heated with delithiated lithium cobaltate, but with less heat and a high reaction temperature. The insufficient thermal stability of the nickelate should be improved for use in practical applications, and trials with partial substitution for nickel are underway.

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