JOURNAL OF APPLIED ELECTROCHEMISTRY **28** (1998) 209–213

Effects of electrolyte composition on the charge and discharge performances of $LiNiO_2$ positive electrode for lithium ion batteries

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Received 1 May 1997; revised 5 July 1997

Charge and discharge behaviour of $LiNiO_2$ positive electrode has been examined in organic electrolytes with different compositions. The discharge capacity of the oxide electrode at a moderate cycling rate varied with the electrolyte composition. Redox responses in potential sweep voltammetry also depended on the kind of lithium salt and solvent of the electrolyte. Electrolyte solutions of relatively low ionic conductivity generally gave lower voltammetric responses and rate capability. A.c. impedance analysis of the $LiNiO_2$ electrode before and after the charge and discharge demonstrated that the surface chemistry of the oxide, depending on the electrolyte composition, has an important influence on the rate capability of the oxide electrode in organic electrolyte solutions.

Keywords: *lithium batteries*, *$LiNiO_2$ positive electrode*, *organic electrolytes*

1. Introduction

A family of $LiMO_2$ (M: transition metal) type oxides is the most attractive for the cathode (positive electrode) material of rechargeable lithium (ion) batteries [1–3]. Among these, lithium nickelate, $LiNiO_2$, is a possible replacement for $LiCoO_2$ cathodes in present lithium ion batteries because the former has higher theoretical capacity and lower cost than the latter [4]. The charge and discharge characteristics of $LiNiO_2$ and related oxides have been investigated in organic electrolyte solutions [5–8]. However, lower cycleability of $LiNiO_2$ than $LiCoO_2$ has prevented its practical use. Basic aspects of the solid state chemistry of this type of oxide have been extensively examined [6, 9, 10]. The substitution of another metal (Co, Mn etc.) for Ni improves the cycleability of the oxide electrode [8, 11]. The electrode reaction of $LiMO_2$ in organic media containing lithium salts is generally considered to be controlled by mass transport (Li^+ diffusion) in the solid phase [4, 10]. However, the performance of batteries with $LiMO_2$ cathodes varies with the electrolyte systems used [12].

It is important to understand the relation between the electrode performance and the electrolyte composition to establish the optimum electrode–electrolyte combination. We have investigated the importance of the electrolyte composition on the characteristics of lithium metal [13, 14] and carbon-based negative [15, 16] electrodes. It is well-known that the electrolyte composition influences the charge and discharge performances of the carbon-based negative electrode [4, 17]. This paper describes the influences of the electrolyte composition on the charge and discharge characteristics of $LiNiO_2$ positive electrodes. The basic behaviour of the oxide electrode has been studied in organic electrolyte solutions consisting of mixed alkyl carbonates and lithium salts. Effects of the solvent and salt on the electrode process are discussed.

2. Experimental details

Mixed solvent systems were used as the electrolytic solution. The high permittivity solvent, ethylene carbonate (EC), or propylene carbonate (PC), was mixed with low viscosity linear alkyl carbonate, dimethyl carbonate (DMC) or diethyl carbonate (DEC) in the volumetric ratio of 50/50. These solvents (Mitsubishi Chemical, Battery Grade) were used as received because the water content in the solvents was below 10 ppm. The electrolytic salts were well-dehydrated $LiClO_4$ (Ishizu Pharmaceutical), $LiPF_6$ (Tomiyama Chemical) and $LiCF_3SO_3$ (Morita Chemical Industries), which were dissolved in the mixed solvents to make 1 M (mol dm^{-3}) solutions. The composition of the electrolyte solution will be ex-

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pressed as 'salt/solvent', e.g. $LiClO_4$/EC + DMC, in this paper. The electrolytic conductivity was measured by an a.c. method using an LCR meter (10 kHz) at 25 °C.

The test electrode consisted of 30 mg of $LiNiO_2$ powder (Nihon Kagaku Sangyo) with 20 mg acetylene black as a conducting support and 5 mg of poly(tetrafluoroethylene) (PTFE) as a binder. These powdered materials were well mixed in a mortar and then pressed onto a current collector screen (a disc of 13 mm diameter) made of stainless steel. The test electrode was dried at 100–120 °C for 5 h or longer under reduced pressure before use.

Fundamental redox responses of $LiNiO_2$ in organic electrolyte solutions were examined by cyclic voltammetry using a conventional three-electrode system. A glass beaker cell equipped with a lithium counter and a lithium reference (Li/Li^+) electrode was used for this experiment. The apparent surface area of the test electrode exposed to the electrolyte solution was 0.95 cm^2. The electrode potential was scanned at the rate of 0.1 or 1.0 $mV\,s^{-1}$. The battery performance of the $LiNiO_2$ positive electrode was investigated by a constant current charge/discharge cycling test using a 2023-size coin cell, in which a lithium metal sheet with a nickel screen backing was used as the counter (negative) electrode. A moderate rate of 1 $mA\,cm^{-2}$ and cut-off voltages of 2.5 and 4.2 V (discharge and charge, respectively) were employed for this cycling test. The cell was cathode-limited in its capacity.

A.c. impedance measurements were also conducted using a three-electrode system. The apparent surface area of the $LiNiO_2$ test electrode in the impedance measurement was reduced to 0.07 cm^2, which was about 1/100 that of the lithium counter electrode, to minimize any influence of the lithium counter electrode on the impedance responses [18]. The frequency was scanned from 65 kHz to 10 mHz with 10 mV a.c. amplitude under o.c.v. conditions before and after the constant current (1 $mA\,cm^{-2}$) charging and discharging. These electrochemical experiments including the electrolyte preparation were carried out under a dry argon atmosphere at room temperature (18–25 °C).

3. Results and discussion

Figure 1 shows typical charge and discharge profiles of $LiNiO_2$ in different solvent systems containing $LiClO_4$. The profiles show the potential variations with the quantity of electricity passed (capacity) at each second cycle. Both charge and discharge capacities depended on the solvent composition under this constant current (1 $mA\,cm^{-2}$) condition. Usually, lower current densities (0.1–0.5 $mA\,cm^{-2}$) are applied to this type of electrode to evaluate the maximum capacity of reversible cycling [5–8]. In this work, we used a rather high current density to investigate the relation between the rate capability of the oxide and the electrolyte composition. With respect to the high permittivity solvent, the discharge capacities in the EC-based electrolytes were higher than those in the PC-based solutions. On the other hand, the low viscosity solvent DMC gave higher capacities than DEC. The capacity of 140 $Ah\,kg^{-1}$ observed in the $LiClO_4$/EC + DMC is equivalent to $x = 0.51$ in the process presented by Equation 1.

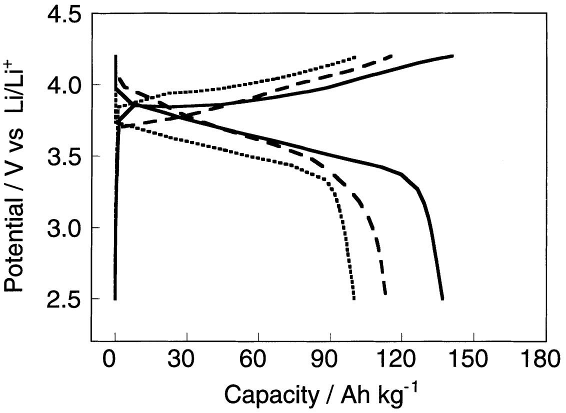

Fig. 1. Charge and discharge profiles of $LiNiO_2$ in different electrolyte solutions containing 1 M $LiClO_4$. Charge and discharge current: 1 $mA\,cm^{-2}$. Solid line: EC + DMC; broken line: EC + DEC; dotted line: PC + DMC.

$$LiNiO_2 = Li_{1-x}NiO_2 + xLi^+ + xe^- \qquad (1)$$

The coulombic efficiency in each charge and discharge cycle was essentially 100% in these $LiClO_4$ solutions.

Figure 2 shows a comparison in the charge and discharge profiles (second cycles) among the electrolyte salts. The discharge capacity in the $LiPF_6$ solution was almost the same as that in the $LiClO_4$ solution, but the $LiCF_3SO_3$ salt lead to lower capacity than the other salts. The discharge capacities in the $LiPF_6$ and $LiCF_3SO_3$ solutions were lower than the corresponding charge capacity. The coulombic efficiencies in these solutions were 80%–85%. As the discharge capacity did not vary when the cycle was repeated, some side reactions in the charging process (e.g. anodic decomposition of the electrolytes) would

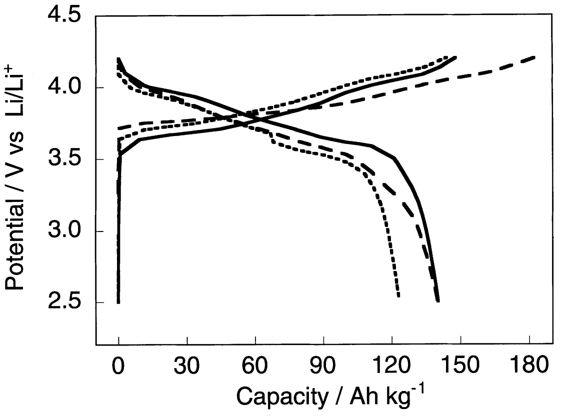

Fig. 2. Charge and discharge profiles of $LiNiO_2$ in EC + DMC based solutions containing 1 M lithium salts. Charge and discharge current: 1 $mA\,cm^{-2}$. Solid line: $LiClO_4$; broken line: $LiPF_6$; dotted line: $LiCF_3SO_3$.

be responsible for the low coulombic efficiencies under this moderate cycling rate condition.

The above results on the influence of the electrolyte composition on the charge and discharge capacities mean that the rate capability of the $LiNiO_2$ electrode depends on the composition of the solution phase. The electrolytic conductivity reflects the structure and motion of ions in the solution. Table 1 summarizes the electrolytic conductivity measured at 25 °C. The order in the conductivity with solvent composition, EC + DEC < PC + DMC < EC + DMC, was common to all salts examined. This tendency is explained by the differences in the permittivity and viscosity among the component solvents. EC has higher permittivity than PC, and DMC gives lower viscosity than DEC. Solutions with higher permittivity and lower viscosity tend to show higher ionic conductivity of its electrolyte solution. The difference in the conductivity among the lithium salts is caused by the differences in the size and shape of the anion.

The order in the discharge capacity of $LiNiO_2$ with respect to the electrolyte composition, shown in Figs 1 and 2, was apparently consistent with that of the conductivity of the electrolyte. This type of electrode reaction, Equation 1, is generally considered to be limited by mass transport processes in the solid phase [4]. Thus, the above results mean that the ionic conductance in the solution phase apparently affects the electrode process in the solid phase.

Figures 3 and 4 show cyclic voltammograms of the $LiNiO_2$ electrode in different electrolyte solutions. The anodic and cathodic current responses correspond, respectively, to the forward (deintercalation; charging) and backward (intercalation; discharging) processes in the Equation 1. With respect to the solvent composition, the current response in the voltammogram increased in the order PC + DMC < EC + DEC ≤ EC + DMC. When a higher potential scan rate (e.g. $1\,mV\,s^{-1}$ or higher) was used, differences in the current response among the solvent composition became much clearer. The order of the anodic and cathodic peak currents in the solutions containing different electrolytic salts was $LiCF_3SO_3 < LiPF_6 \simeq LiClO_4$ (Fig. 4). These results on the current responses in voltammetry were almost consistent with those obtained by constant current charge and discharge cycling tests.

The influence of the electrolyte composition on the electrode process of $LiNiO_2$ was further investigated by an a.c. impedance technique. Complex-plane impedance plots (Cole–Cole plots) are given in Figs 5 and 6. The difference in the electrolytic conductivity of the solution is primarily reflected in the intersection of the plot at the Z' axis. The impedance measured at 0.5 h after the cell assembly (plots a) showed almost linear relations, suggesting that the electrode system is controlled by diffusion processes. After charging to 4.2 V, the impedance plot gave a semicircle (plots b) for each electrolyte composition, which means that a charge transfer step may participate in the charging (deintercalation) process in these electrode/electrolyte systems. The size of the semicircle (i.e. the charge transfer resistance) became generally large after discharge to 3.6 V (plot c) in each electrolyte system. With respect to the electrolytic salt, the resistive component after the discharge (plot c) increased in the order $LiClO_4 < LiPF_6 < LiCF_3SO_3$ (Fig. 5). Among the solvent compositions (Fig. 6), the resistance observed in EC + DMC was almost the same as that in EC + DEC. However, the size and shape of the semicircle obtained in PC + DMC was different from that in EC + DMC.

Table 1. Electrolytic conductivity of the carbonate-based solutions containing 1 M lithium salts at 25 °C

Electrolytic salt (1 M)	*10^3 Conductivity/S cm^{-1} Solvent (50/50 by volume)*		
	EC + DMC	*EC + DEC*	*PC + DMC*
$LiPF_6$	11.2	7.8	10.0
$LiClO_4$	10.1	6.4	6.8
$LiCF_3SO_3$	3.1	2.1	2.2

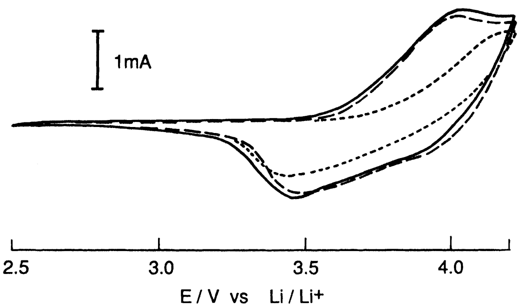

Fig. 3. Potential sweep voltammograms of $LiNiO_2$ in different electrolyte solutions containing 1 M $LiClO_4$. Potential sweep rate: $0.1\,mV\,s^{-1}$. Key: (——) EC + DMC; (- - - -) EC + DEC; (· · · · · ·) PC + DMC.

Generally the electrode process of $LiMO_2$ type oxides (M = Co, Ni) in organic solutions containing lithium salts, as shown in Equation 1, is considered to be controlled by the diffusion of lithium in the solid phase. As shown in Figs 1 and 2, however, the charge and discharge characteristics depend greatly on the electrolyte composition. Further, the results shown in Figs 5 and 6 suggest that certain resistive components at the electrode/electrolyte interface play important roles in the charge and discharge processes. It is likely

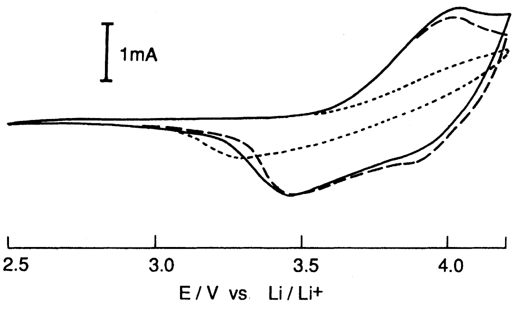

Fig. 4. Potential sweep voltammograms of $LiNiO_2$ in EC + DMC based solutions containing 1 M lithium salts. Potential sweep rate: $0.1\,mV\,s^{-1}$. Key: (——) $LiClO_4$; (- - - -) $LiPF_6$; (· · · · · ·) $LiCF_3SO_3$.

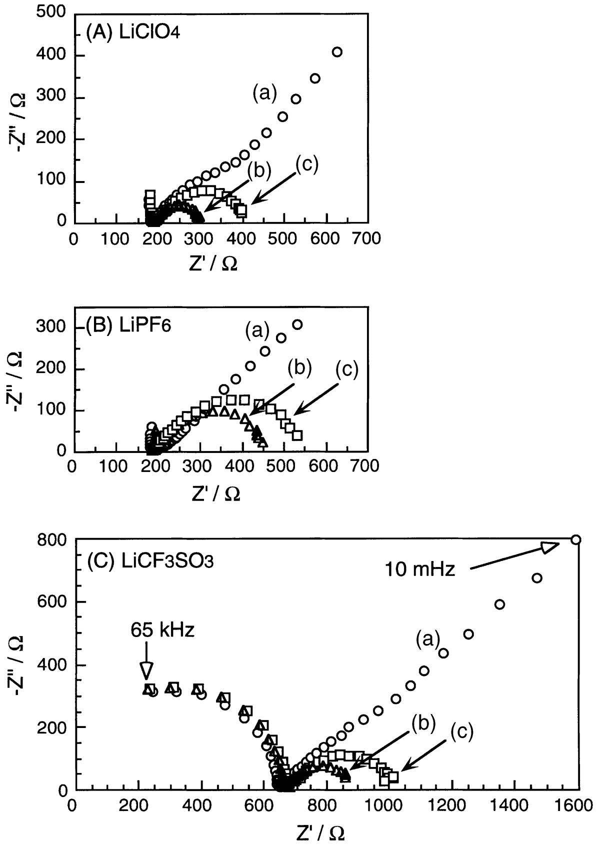

Fig. 5. Cole–Cole plots for a.c. impedance obtained for $LiNiO_2$ in EC + DMC based solutions containing 1 M lithium salts. (A): $LiClO_4$, (B): $LiPF_6$, (C): $LiCF_3SO_3$. Plot (a): before the cycle; plot (b): after the charge to 4.2 V; plot (c): after the discharge to 3.6 V.

that a film formation reaction on the oxide surface is responsible for these resistive components, which may control the rate capability of the oxide electrode. Another possible explanation is that the activity of the Li^+ species in the solution, depending on the solution composition, affects the resistance component of the impedance at the electrode/electrolyte interface. On the other hand, Kanamura *et al.*, reported that the reactivity of the electrolyte solution and the resulting products at the oxide formed on a nickel substrate varied with the electrolyte salt in PC-based systems [19]. Similarly, differences in the reactivity of the solution on $LiNiO_2$ possibly relate to differences in the interface resistance. The results on the discharge capacity and the coulombic efficiency in the cycle are qualitatively consistent with those obtained from the impedance measurements. That is, the electrolyte system showing the lower interface resistance gave the higher discharge capacity and/or the higher coulombic efficiency.

4. Conclusion

The charge and discharge characteristics of $LiNiO_2$ positive electrodes depended on the composition of organic electrolytes based on mixed alkyl carbonates. The discharge capacity of the oxide electrode at a moderate cycling rate increased in the order PC + DMC < EC + DEC < EC + DMC for the solvent and $LiCF_3SO_3 < LiPF_6 \leq LiClO_4$ for the salt. Potential sweep voltammetry supported these trends in the activity of the oxide in the organic electrolytes. Electrolyte solutions whose ionic conductivities are relatively low generally gave lower voltammetric responses and rate capability. A.c. impedance analysis of the oxide electrode before and after charge and discharge demonstrated that the surface chemistry of the oxide depends on the electrolyte composition and then affects the rate capability of the electrode in organic electrolyte solutions.

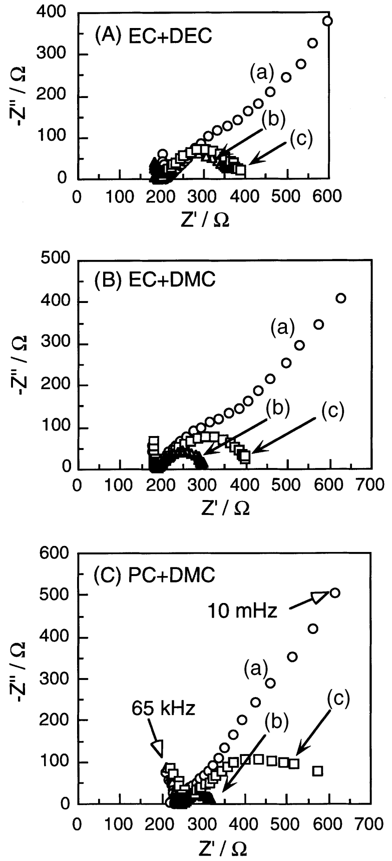

Fig. 6. Cole–Cole plots for a.c. impedance obtained for $LiNiO_2$ in different electrolyte solutions containing 1 M $LiClO_4$. (A): EC + DMC; (B): EC + DEC; (C): PC + DMC. Plot (a): before the cycle; plot (b): after the charge to 4.2 V; plot (c): after the discharge to 3.6 V.

Acknowledgements

This work was financially supported by Grant-in-Aid for Scientific Research (08650980, 09237250) from the Ministry of Education, Science, Sports and Culture. The authors thank Nihon Kagaku Sangyo, Co. Ltd, for supplying the oxide sample.

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