EFFECT OF SODIUM CATION ON LITHIUM CORROSION IN APROTIC MEDIA

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Summary

The present paper discusses the effect of Na^+ on the characteristics of lithium cells. The lithium cycling efficiency and the capacity retention of cathodically deposited lithium and of Li/MnO_2 and Li/Bi_2O_3 cells are much lower in electrolytes containing Na^+. This deterioration in characteristics is accounted for by an enhancement of lithium anode corrosion in the presence of Na^+ in the electrolyte. The corrosion mechanism is described.

Introduction

The nature of the electrolyte has a considerable and, in some cases, a determining influence on the characteristics of lithium cells. The most important objective in preparing electrolyte solutions is water removal to prevent lithium corrosion and other unfavourable effects. Most of the water is removed during the distillation of the solvent and the drying of the salt. Some salts (*e.g.*, $LiBF_4$), however, do not always lend themselves to sufficient drying by the usual calcination methods and, therefore, the solutions must also be dried. The use of sodium zeolites for this purpose leads to an exchange of some of the Li^+ ions in the electrolyte with Na^+ ions [1]. Lithium cycleability is thereby reported to be impaired [2] and the characteristics of the Li/-MnO_2 cell deteriorate [3] after treatment of the electrolyte solution with zeolites.

This work is an attempt to determine how, and to what extent, Na^+ influences lithium corrosion and the characteristics of primary and secondary cells.

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Experimental

The following electrolytes were used:
(i) 1 M $LiBF_4$/γ-butyrolactone (BL), 230 ppm H_2O
(ii) 1 M $LiBF_4$/BL, <100 ppm H_2O
(iii) 0.68 M $LiBF_4$ + 0.32 M $NaBF_4$/BL, 80 ppm H_2O
(iv) 0.68 M $LiBF_4$ + 0.32 M $NaBF_4$/BL, 230 ppm H_2O
(v) 0.36 M $LiBF_4$ + 0.17 M $NaBF_4$/BL, 200 ppm H_2O
(vi) 1 M $LiClO_4$/propylene carbonate (PC) ⎤
(vii) 0.9 M $LiClO_4$ + 0.1 M $NaClO_4$/PC   ⎪
(viii) 1 M $NaClO_4$/PC   ⎬ <100 ppm
(ix) 1 M $NaClO_4$/BL   ⎪ H_2O
(x) 1 M $LiClO_4$/BL   ⎦

The electrolytes were prepared from twice-distilled solvents containing less than 40 ppm H_2O. Electrolyte (ii) was produced by drying electrolyte (i) with lithium amalgam and electrolyte (iii) by drying electrolyte (i) over the synthetic zeolite NaA-2MIII. The Na^+ concentration in the electrolyte was determined by flame photometry. Electrolyte (iv) was produced from electrolyte (iii) by adding water to give a 230 ppm concentration. Electrolyte (v) was obtained by dissolving dried $NaBF_4$ and $LiBF_4$ salts in the solvent. The electrolyte water concentrations were determined by the Karl Fischer method.

The lithium cycling experiments and experiments for determining lithium capacity retention were carried out on a 0.1 mm-thick nickel foil of 1 cm^2 area. Two auxiliary electrodes were made of lithium pressed on a nickel net of 1.44 cm^2 area.

The electrodes were stacked and placed in the slot of a Teflon rod, which could be tightly inserted into an hermetically sealed glass cell; the electrodes were separated by a thin glass fibre separator. The volume of the electrolyte was less than 1.5 ml. All the potential values in the paper are reported against a lithium reference electrode.

Lithium was deposited galvanostatically during cycling at a current density of 1 mA cm^{-2} and at a charge of 1 C cm^{-2} in each cycle. After charging, discharge took place at the same current density until 0.3 V potential was reached. The cycling efficiency was determined as discharge/charge capacity ratio for each cycle.

To determine capacity retention, 10.8 C cm^{-2} of metal were deposited onto a nickel foil at 1 mA cm^{-2} current density. Each electrode was then stored in the electrolyte for a known time and discharged at 1 mA cm^{-2} to 0.5 V. The electrode's capacity retention was estimated from the dependence of single cycle efficiency on the time it was stored in the electrolyte between charging and discharging.

Lithium/MnO_2 and Li/Bi_2O_3 coin cells were constructed. After assembly, the Li/MnO_2 cells were partly discharged into a 5.6 kΩ load for 8 h. This was done to remove the primary lithium-permeable film, formed in the gas atmosphere during production of the electrode, from the lithium surface.

Another film, related to the electrolyte properties, formed during storage.

Standard electrochemical equipment was used for the cyclic voltammetry and the polarization studies. Special equipment was used for galvanostatic cycling experiments.

All cell assembly operations and experiments were undertaken in air dried over P_2O_5.

Effect of sodium cation on the cycleability of lithium and the retention of its capacity

Almost all solvents employed in lithium cells are oxidants towards lithium [1]. Lithium dissolves in them to form a film of corrosion products. Freshly deposited lithium has the highest activity towards the electrolyte components. The film formed on it depends entirely on the nature of the electrolyte. This film determines the main characteristics of the lithium electrode, including the cycleability of lithium and the retention of its capacity.

As seen in Fig. 1, different electrolytes exhibit different cycling efficiencies. In electrolytes (iii) - (v) containing Na^+, the cycling efficiency decreases rapidly to values below 15%. After stopping cycling for 16 h, during which time the electrode remained under open circuit conditions, cycling was renewed. The lithium oxidation process, however, occurred at potentials
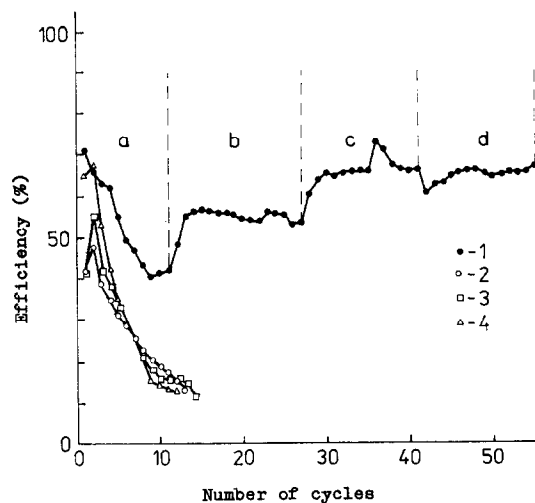

Fig. 1. Efficiencies of cycling Li on a Ni substrate as a function of the number of cycles and electrolyte composition: 1, 1 M LiBF$_4$/BL, 230 ppm H$_2$O; 2, 0.68 M LiBF$_4$ + 0.32 M NaBF$_4$/BL, 80 ppm H$_2$O; 3, 0.68 M LiBF$_4$ + 0.32 M NaBF$_4$/BL, 230 ppm H$_2$O; 4, 0.36 M LiBF$_4$ + 0.17 M NaBF$_4$/BL, 200 ppm H$_2$O. a, b, c, d: cycling series with 16 h breaks.

above the cutoff potential due to an appreciable overpotential, and it was impossible to obtain more capacity from the electrode. In electrolyte (i), without Na^+, lithium was cycled with higher efficiency. Holding the electrode under open circuit conditions for 16 h between the cycling series a, b, c, and d did not decrease the cycling efficiency. On the contrary, it tended to increase at stabilized cathodic and anodic overpotential values.

The following considerations support the conclusion that the poorer lithium cycleability in electrolytes (iii) - (v) is due to the presence of Na^+: Water concentration variation over the range 80 - 230 ppm does not substantially affect the cycling efficiency. The similar shapes of curves 2 and 3 of Fig. 1 support this. Electrolytes (i) and (iv) contain the same amounts of water but differ in Na^+ content although curves 1 and 3 of Fig. 1, obtained in these electrolytes, differ greatly. Other possible impurities which worsen the lithium cycleability may be expected to pass from the zeolite to the electrolyte during zeolite treatment. This is, however, not the case since electrolyte (V), containing Na^+, was not treated with zeolite, yet its performance was as poor as those which had been so treated. Thus the poorer lithium cycleability in electrolytes (iii) - (v) can only be attributed to Na^+.

The composition of the electrolyte also directly affects the capacity retention of cathodically deposited lithium. As seen in Fig. 2, the decrease in capacity with time in electrolyte (ii) is smaller than that in electrolyte (i). It is possible that this is due to the oxidant impurities in electrolyte (i), which cause lithium electrode corrosion, being destroyed during electrolyte treatment with lithium amalgam. At the same time, the capacity of the cathode deposit in electrolyte (iii), which contains negligible water, decreases rapidly with time. The only significant difference between electrolytes (ii) and (iii) is the presence of a considerable amount of Na^+ in the latter.

According to chemical analysis data, the metal deposited cathodically from electrolyte (iii) contained mainly lithium and less than 1 at.% of sodium.
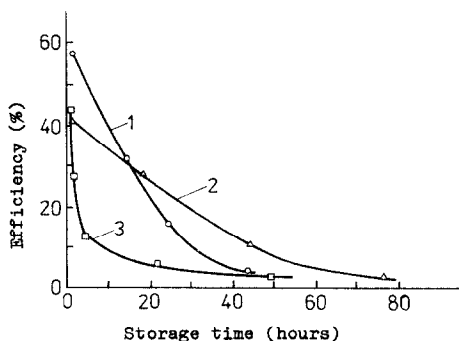

Fig. 2. Single cycle efficiency of cathodically deposited Li as a function of its storage time and electrolyte composition. 1, 1 M $LiBF_4$/BL, 230 ppm H_2O; 2, 1 M $LiBF_4$/BL, less than 100 ppm H_2O; 3, 0.68 M $LiBF_4$ + 0.32 M $NaBF_4$/BL, 80 ppm H_2O.

The data obtained indicate an adverse effect of Na^+ on the capacity retention of cathodically deposited alkali metal and on lithium electrode cycleability. This is due to the higher alkali metal corrosion rate in the sodium-containing electrolyte. A possible mechanism is that the cycling efficiency and capacity are decreased not so much by lithium dissolution during corrosion as by the encapsulation of individual lithium grains by reaction products which prevent them from participating in the discharge process.

To elucidate the mechanism of lithium corrosion in the presence of Na^+ we have studied the behaviour of a sodium electrode in electrolytes (ii) and (iii). A cyclic voltammogram for a sodium electrode in electrolyte (ii) is shown in Fig. 3. The curve for electrolyte (iii) has a similar shape. The sodium potential on dipping in the electrolytes was -0.41 V. When the potential was shifted from the initial value towards more positive values, an anode current increase was observed, which is logically attributed to a sodium oxidation process. A characteristic current increase takes place at negative potentials associated with lithium deposition on the electrode. When the potential is reduced, an anodic wave with a maximum, typical of the lithium oxidation process, appears. The voltammogram (Fig. 3) shows an extremely small current in the potential range $0 - 0.4$ V, which most likely corresponds to Na^+ reduction from the electrode layer. It is surprising, however, that the cathode current of Na^+ reduction in electrolyte (iii) also has a low value, despite the high Na^+ concentration, and does not exceed 0.15 mA cm^{-2}. This can, however, be explained: sodium is known to interact with solvents to a greater extent than lithium [4]. A freshly scraped, bright sodium surface becomes dull in the electrolyte within several minutes whereas lithium remains bright for an extended period of time. It is the corrosion film products on sodium that determine the low limiting rate of the sodium reduction process. The film does not hinder the diffusion of
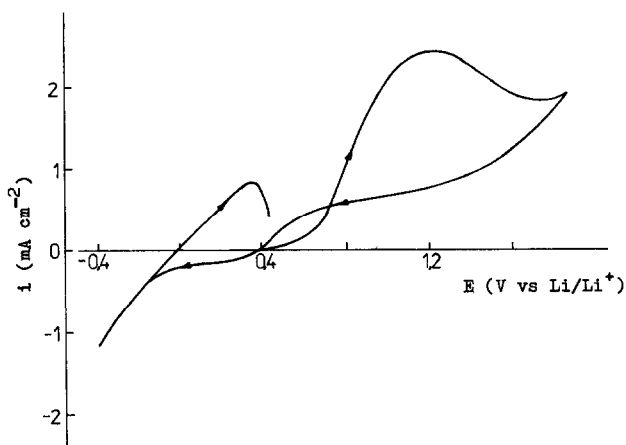

Fig. 3. Cycling voltammogram for a Na electrode in 1 M LiBF$_4$/BL (<100 ppm H$_2$O). Potential sweep rate: 80 mV s^{-1}.

much smaller Li^+ ions to the electrode at cathodic-deposition potentials. The considerable slope of the lithium deposition voltammogram, however, indicates a high film resistance.

It follows from the experiments carried out that, under the present conditions, sodium is less electronegative than lithium. Hence, it deposits first during electrolysis. The low sodium reduction rate does not, however, permit the production of sodium on the cathode in large quantities. This agrees with the chemical analysis data for the metal deposited on the cathode from electrolyte (iii). Lithium also displaces sodium from the sodium salts dissolved in the electrolyte through a contact exchange. Since sodium displaced in this way interacts at a higher rate with the electrolyte, the lithium grain "encapsulation" rate in the metal deposit increases. The overpotential of the process also increases owing to the high resistance of the film of sodium corrosion products.

Capacity retention of primary cells

The above lithium corrosion mechanism is valid for both secondary and primary chemical cells with freshly deposited lithium. The process occurs, however, at a much lower rate owing to the much smaller reaction surface of lithium. As the discharge characteristics of Figs. 4, 5, and Table 1 show, the capacity of cells containing Na^+ in the electrolyte is far lower than that of cells free from Na^+. All cells with Na^+ ions in the electrolyte exhibited reduced shelf life at 50 °C. In accordance with the above mechanism this is due to the anode corrosion products increasing the internal cell resistance
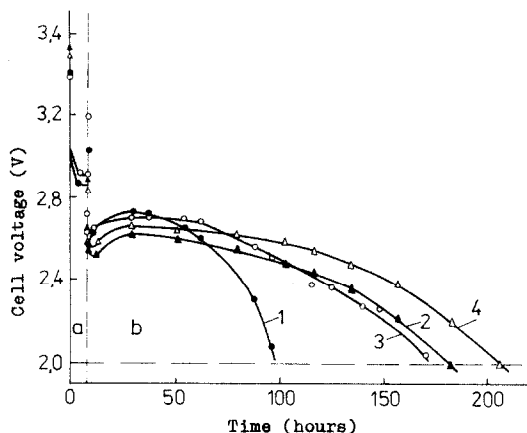

Fig. 4. Discharge characteristics of Li/MnO_2 coin cells as a function of electrolyte composition. 1, 2, 0.68 M $LiBF_4$ + 0.32 M $NaBF_4$/BL, 80 ppm H_2O; 3, 4, 1 M $LiBF_4$/BL, < 100 ppm H_2O. Storage conditions: 1, 3, 7 days at T = 20 °C, then 62 days at T = 50 °C; 2, 4, 45 days at T = 20 °C, then 20 days at T = 50 °C, a, before storage; b, after storage; load resistance: 5.6 kΩ.
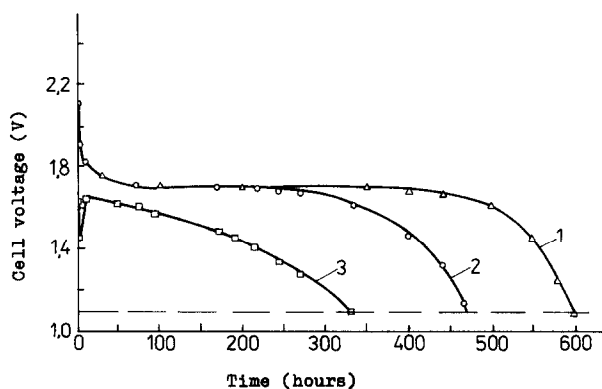
Fig. 5. Discharge characteristics of Li/Bi$_2$O$_3$ coin cells as a function of electrolyte composition. 1, 1 M LiClO$_4$/PC; 2, 0.9 M LiClO$_4$ + 0.1 M NaClO$_4$/PC; 3, 1 M NaClO$_4$/PC. Water content of the electrolytes: <100 ppm; load resistance: 5.6 kΩ.

TABLE 1

Capacities of lithium cells with different cathodes, electrolytes, and storage conditions

Chemical cell	Electrolyte	Capacity after storage (mA h)		
		at 20 °C 45 days, then at 50 °C 20 days	at 20 °C 7 days, then at 50 °C 62 days	at 20 °C 3 days
Li/MnO$_2$ discharge to 2.0 V	1 M LiBF$_4$/BL	90	75	
	0.68 M LiBF$_4$ + 0.32 M NaBF$_4$/BL	78	47	
Li/Bi$_2$O$_3$ discharge to 1.1 V	1 M LiClO$_4$/PC			180
	0.9 M LiClO$_4$ + 0.1 M NaClO$_4$/PC			146
	1 M NaClO$_4$/PC			86

during discharge to a greater extent when using the sodium-containing electrolyte (iii) than when using electrolyte (ii).

The greater decrease in the capacity of the Li/MnO$_2$ cell with sodium-containing electrolyte could be accounted for by inhibition of the topochemical implantation of larger Na$^+$ into the cathode lattice. The adverse effect distinctly manifests itself, however, when hermetically-sealed Li/Bi$_2$O$_3$ coin cells are discharged. Bismuth oxide is reduced by a disproportionation mechanism to form metallic bismuth and alkali metal oxide. The Bi$_2$O$_3$ reduction potential in sodium electrolyte (ix) is somewhat lower than in lithium electrolyte (x), but the capacity is practically the same when discharging the cathode to 1.0 V (Fig. 6). Therefore the decrease in Li/Bi$_2$O$_3$
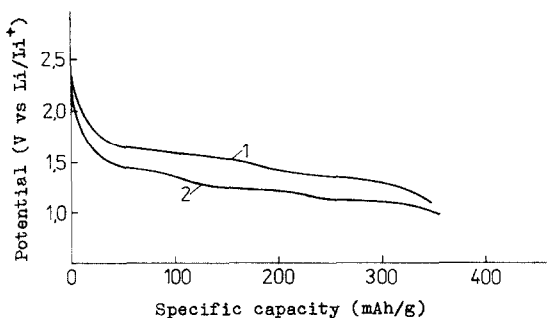
Fig. 6. Discharge characteristics of a Bi_2O_3 cathode at 0.3 mA cm^{-2} drain as a function of the nature of the electrolyte. 1, 1 M LiClO$_4$/BL, lithium counter electrode; 2, 1 M NaClO$_4$/BL, sodium counter electrode; water content of the electrolyte: <100 ppm.

cell capacity in the presence of Na$^+$ cannot be accounted for by the lower cathode reduction potential.

The lower voltage of cell 3 (Fig. 5) may be due to the lower thermodynamic cathode reduction potential in sodium electrolyte (viii) and to the higher overpotential of lithium oxidation on the anode caused by a denser film of corrosion products. A characteristic voltage drop at the beginning of discharge indicates, in addition to the previous experiments, the existence of such a film of corrosion products. Cells 1 and 2 have no such voltage drop since the electrolyte either contains no Na$^+$ (cell 1) or its concentration is low (cell 2).

It should be noted that Li/Bi$_2$O$_3$ cells were discharged after three days of storage at 20 °C. When the cells are stored for a longer period, especially at an elevated temperature, all exhibit voltage drops, and the capacity loss of cells with Na$^+$ in the electrolyte is greater.

One of the possible reasons for the cell capacity decrease may be positive current-collector corrosion. This possible process in Li/MnO$_2$ cells, however, is suppressed by partial discharge. The corrosion of the positive current-collector is impossible in cells with 1.5 V voltage since the open circuit voltage after assembly is 2.2 V. Thus decreased cell capacity manifests itself when using different cathodes with differing solvents and salt anions.

Conclusions

The presence of Na$^+$ in an electrolyte solution adversely affects the characteristics of lithium cells through anode corrosion. The process is more pronounced in secondary cells. This makes the use of electrolytes containing Na$^+$ in rechargeable cells very undesirable.

The adverse effect of Na$^+$ sould be taken into account when choosing the method for drying electrolytes.

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