

**EFFECT OF SODIUM CATION ON LITHIUM CORROSION
IN APROTIC MEDIA (EXTENDED ABSTRACT)**

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When lithium salt solutions are dried with sodium zeolites, a cation exchange takes place and, as a result, cations pass to the electrolyte.

Since practically all solvents used in lithium chemistry cells are oxidants towards lithium and form a film of corrosion products on the surface by reaction with lithium, it was considered interesting to determine the effect of sodium cations on the lithium corrosion process in chemical cells.

To elucidate the situation, plots of lithium cycling efficiency variations *versus* the number of cycles in LiBF_4 -in- γ -butyrolactone solutions, have been obtained in the presence and absence of sodium cations. In the absence of sodium cations in the electrolyte, the lithium cycling efficiency is 40 - 70% over dozens of cycles. In electrolytes containing varying amounts of sodium cations, the efficiency decreases rapidly, from 40 - 70% to 15%, over fifteen cycles and it is not restored when cycling is renewed after keeping the electrode under currentless conditions.

The plots obtained, of lithium cycling efficiency variation against lithium storage time between charge and discharge operations in electrolytes with and without sodium cations, indicate a much lower retention of cathodically deposited lithium capacity in those electrolytes containing sodium cations.

The capacity values of the Li/MnO_2 and $\text{Li/Bi}_2\text{O}_3$ coin cells listed in Table 1 are much lower when an electrolyte containing sodium cations is used.

The results obtained indicate that sodium cations have an adverse effect on lithium cell capacity. This is due to the higher rate of reaction between lithium and electrolyte containing sodium cation. The mechanism of lithium corrosion in the presence of sodium cation in the electrolyte can be represented as follows: the equilibrium potential of a sodium electrode is positive relative to the lithium electrode potential (+0.41 V in 1 M $\text{LiBF}_4/\gamma\text{-BL}$). Because of this, sodium deposits on the lithium surface through contact exchange. Sodium reacts with the solvent at an increased rate and forms a film of corrosion products which has a low lithium ion conductivity; this increases the rate of lithium grain encapsulation. The process is pronounced in secondary cells since cathodically-deposited lithium is especially

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TABLE 1

Capacity 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 /γ-BL	90	75	
	0.68 M LiBF ₄ + 0.32 M NaBF ₄ /γ-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

active towards the solution components. The process also manifests itself in primary cells having different cathodes, and with the solvent and salt of different natures, but it occurs at a much lower rate due to the much smaller reaction surface of lithium and to its possible initial protection by the primary lithium ion conducting film formed in the gaseous atmosphere during electrode manufacture.

The adverse effect of sodium cation on the cyclability of the negative electrode, and the retention of primary and secondary chemical lithium cell capacity, should be taken into account when deciding on the method of drying electrolytes.