

# DIOXOLALE ELECTROLYTE FOR LITHIUM-ION BATTERIES: PROBLEM OF POLYMERISATION

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## Introduction

Lithium-ion batteries are rather sophisticated electrochemical systems. The majority of commercialized batteries are used solutions of  $\text{LiPF}_6$  in ethylene-carbonate-based mixtures as electrolytes. Such electrolytes have certain drawbacks, what leads to the intensive search for new electrolytes until very recently. One of promising alternative electrolyte could be solution of  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$  in 1,3-dioxolane (DO). Indeed, anion  $\text{N}(\text{CF}_3\text{SO}_2)_2^-$  is more stable and can't be origin of harmful HF. Sadly, DO is known to be prone to polymerization [1, 2], although experimental data on this phenomenon are far and few between. In this work electrochemical behavior of current-collectors from nickel, stainless steel, and aluminum in 1M  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$  in DO is studied.

## Experimental

The measurements were conducted in three-electrode glass cells with counter and reference electrodes made from Li-foil. Cyclic voltammetry and electrochemical impedance spectroscopy were used. The cycling voltammograms (CVs) were recorded in potential range from 2.5 to 6.0 V vs.  $\text{Li/Li}^+$  (depending on material of working electrode) with a potential scan rate of 1 mV/s. The impedance spectra were obtained in the frequency range from 1 Hz to 100 kHz.

Besides  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$  solution in DO, similar solutions in mixtures of DO + propylene carbonate (PC) and DO + dimethoxyethane (DME) were studied.

## Results and discussion

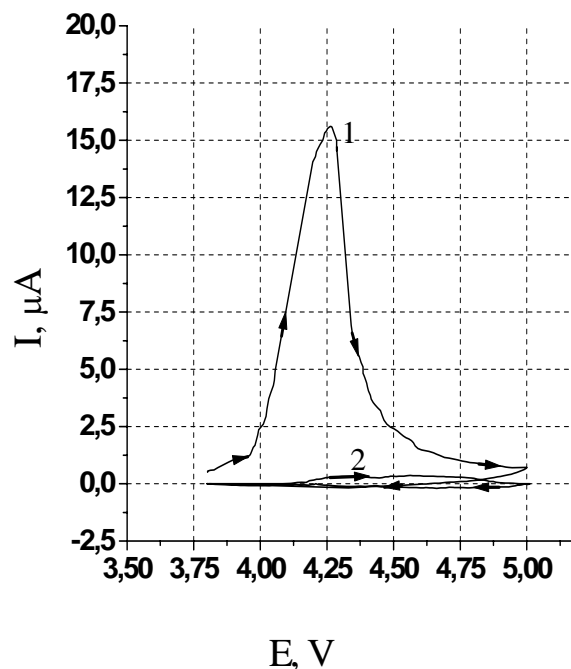
Fig. 1 shows CVs for the 1st and 2nd cycles of the Ni electrode in 1M  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$  + DO. An irreversible peak in the vicinity of 4.25 V was observed during the 1st anodic polarization. Simultaneously some colorless viscous mass was formed on work electrode surface. Obviously, polymerization of DO took place in this case, and this very phenomenon caused electrode "passivation".

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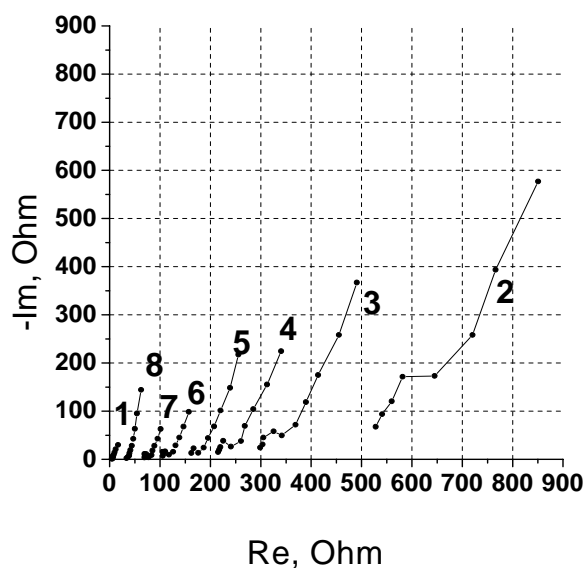
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**Fig. 1** Cyclic voltammograms of Ni electrode in 1M  $\text{LiN}(\text{CF}_3\text{SO}_2)_2 + \text{DO}$  for 1st and 2nd cycles.

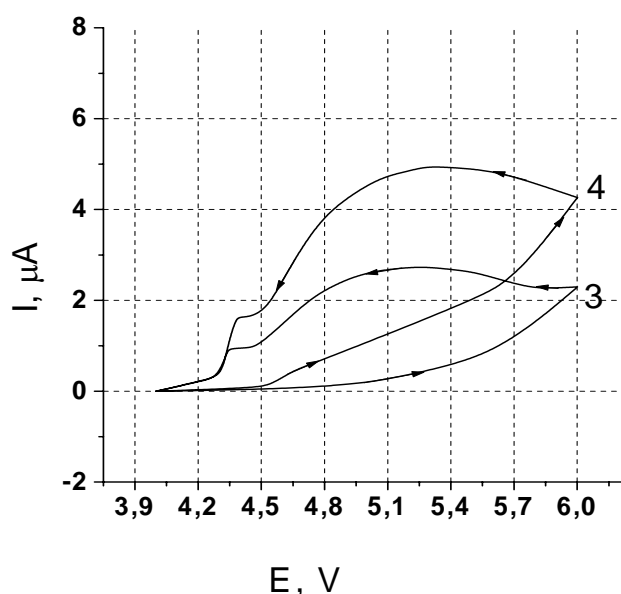
The high frequency portions of impedance spectra for fresh Ni electrode, and for this electrode after 1<sup>st</sup> cycle and after storage for various times are shown at Fig. 2. The intersection of the portions with x-axis can be considered as electrolyte ohmic resistance  $R$ . After 1<sup>st</sup> cycle  $R$  was increased by more than 50 times. During following storage values of  $R$  was returned to initial one. This pointed to dissolution of polymer formed in the course of the 1<sup>st</sup> cycle. This fact was confirmed also with visual inspection.



**Fig. 2** The impedance spectra for fresh Ni electrode (1), and for the electrode after the first polarization (2) and after storage for 20 min. (3), 40 min. (4), 60 min. (5), 80 min. (6), 120 min. (7), and 240 min. (8) in 1M  $\text{LiN}(\text{CF}_3\text{SO}_2)_2 + \text{DO}$ .

The behavior of dioxolane electrolyte at stainless steel electrode was on the whole similar to that at Ni electrode but anodic peak in CVs was shifted into positive direction up to 4.6 V. Process of DO polymerization, as well of electrode passivation took place too. The impedance spectra for stainless steel electrode were also similar to those for Ni.

Quite another picture was observed, when a working electrode was made from aluminum. There was no noticeable anodic current in the potential range from 3.4 to 5.0 V. The anodic current rise appeared only at potentials more positive than 5.0 V, and the current became more and more from one cycle to another (Fig. 3). It is interesting to note that we can notice a product of DO polymerization only at potentials more positive than 6.5 V.



**Fig. 3** Cyclic voltammograms of the Al electrode in 1M LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub> + DO for 3<sup>rd</sup> and 4<sup>th</sup> cycles

One could believe that adding other solvents to DO would hinder polymerization. Sadly, this was far from being the case. Changing mixtures DO + PC or DO + DME for plain DO didn't prevent polymerization, and moreover in some cases this phenomenon manifested itself yet more.

## Conclusion

Dioxolane subjected to polymerization in the course of anodic polarization and polymerization rate is strongly depends on the nature of anode.

## References

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