



Influence of Aprotic Solvents on Negative Electrode Material Properties for Lithium-ion Batteries

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Abstract:

The following article focuses on the safety and stability of lithium-ion batteries. This type of aprotic battery is of high quality, and known to offer a number of advantages. Generally, they are used in small portable devices, such as cell phones, laptops and other similar applications. Lithium-ion batteries seem to be suitable for use in electric vehicles, in particular due to their high specific energy density. This unusual application of lithium-ion batteries puts specific demands on their parameters, e.g. high cyclability, temperature stability, etc. In this article, we have focused on materials for negative electrode along with aprotic solvents. Currently, the majority of commercially used lithium-ion batteries have a negative electrode made from graphite material with specific capacity of 372 mAh/g. As an appropriate successor of graphite, it can be considered a spinel Lithium-Titanate-Oxide (LTO), with theoretical capacity of 175 mAh/g. The liquid electrolyte solvents for lithium-ion batteries should be safe in conditions requiring high performance applications. Among important parameters of aprotic solvent belong thermal resistibility, high flash point and compatibility with electrode materials. In our experiments we used organic solvents, ethylene carbonate, dimethyl carbonate and sulfolane.

Keywords:

Battery, Lithium, Safety, Capacity, LTO

1. Introduction

At the present time, lithium-ion batteries use graphite materials which act as a negative electrode intercalation host for Li atoms. Graphite plays a major role in the field of

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negative electrode materials for lithium-ion batteries. Due to the wide-spread use of lithium-ion batteries in a large range of applications, they have been developed for small portable electronic devices, as well as high powered applications, such as the propulsion of electric vehicles. New applications for lithium-ion batteries make higher demands on lithium-ion cell capacity, performance capability, safety, stability, etc. Especially in cases of high current loading of lithium-ion cell, there occurs a non-reversible degradation of graphite material and graphite solid/liquid interface layer. Graphite electrode performance drop is given by thermal runaway in electrode bulk, relating to graphite expansion. This process results in a significant decrease of cell performance capability, capacity and also a risk of electrolyte product ignition. This point of view raises the question of lithium-ion battery fire safety focused on thermal resistivity and the stability of the aprotic electrolyte that is used. Development of new materials with improved characteristics brings plenty of questions regarding the mutual compatibility of single cell components as electrode and electrolyte. This research work briefly describes an experiment with negative electrode materials and aprotic solvents with higher fire safety in a system of lithium-ion battery. Graphite is made up by graphene sheets which are spaced apart 0.335 nm. The main principle of negative electrode operation lies in the intercalation ability. During the charging process, the lithium atoms (cations) diffuse into graphene layers to give an origin of non-stoichiometric compound LiC_6 . This intercalation phenomenon causes graphite volume to increase about 10 %. The theoretical capacity of graphite (LiC_6) is 372 mAh/g in comparison with formerly used metal lithium (3 860 mAh/g), which was replaced by graphite due to its instability being significantly lower. Compared with graphite anode, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) is considered a promising alternative because of its excellent reversibility and stability. This stability of LTO is associated with the electrochemical inertness in common organic electrolytes. The redox potential of LTO is 1.55 V vs. Li^+/Li , at which neither electrolyte oxidation nor reduction reaction occurs. The theoretical LTO capacity is 175 mAh/g which is significantly less than that of graphite. Side reactions related to LTO electrode and their influence on the cyclability will be minimized. The high Li intercalation voltage also suppresses the growth of hazard lithium dendrites and formation of Solid Electrolyte Interface (SEI) film. These characteristic properties make LTO a very interesting anode material for lithium-ion batteries. The solvent that was chosen for increasing the fire safety in batteries was sulfolane. Sulfolane is an aprotic solvent containing sulphur which is known for its high dielectric constant 46.4 (-), high flashpoint 166 °C and boiling point 280 °C. Sulfolane also has a high cryoscopy constant 65.5 $\text{K}\cdot\text{kg}\cdot\text{mol}^{-1}$ and high oxidation potential approx. 5.3 V. Other benefits are stability, good conductivity under higher temperatures, related higher capacity and rate-capability performance. The batteries which use common carbonaceous organic solvents mixture (ethylene carbonate and dimethyl carbonate) have better conductivity in lower temperatures [1 – 6].

2. Experiments

The following sections describe the experiments focused on negative electrode materials and aprotic solvents. Two kinds of negative electrode materials were used in the experimental work, which are also found in lithium-ion batteries. Most widely used natural graphite grade CR5995 and spinel-type LTO. The electrolyte used in all cases was 1 M solution of LiPF_6 at given solvent. Two electrolytes were prepared, the

first one was represented by common ethylene carbonate – EC and dimethyl carbonate – DMC solvents mixture which were blended in 50 wt % to 50 wt % ratio gives EC/DMC solvents mixture. As a second electrolyte was used pure sulfolane – SUL, this solvent has a significantly higher flash (thermal resistivity) point (165 °C) in comparison with EC/DMC mixture whose flash point lies in approx. 60 °C.

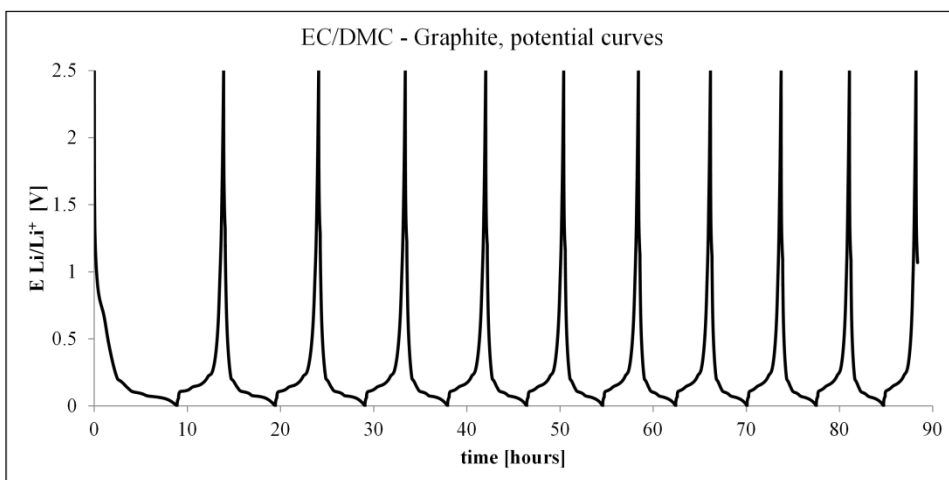


Fig. 1. Charge-discharge characteristics of natural graphite CR5995

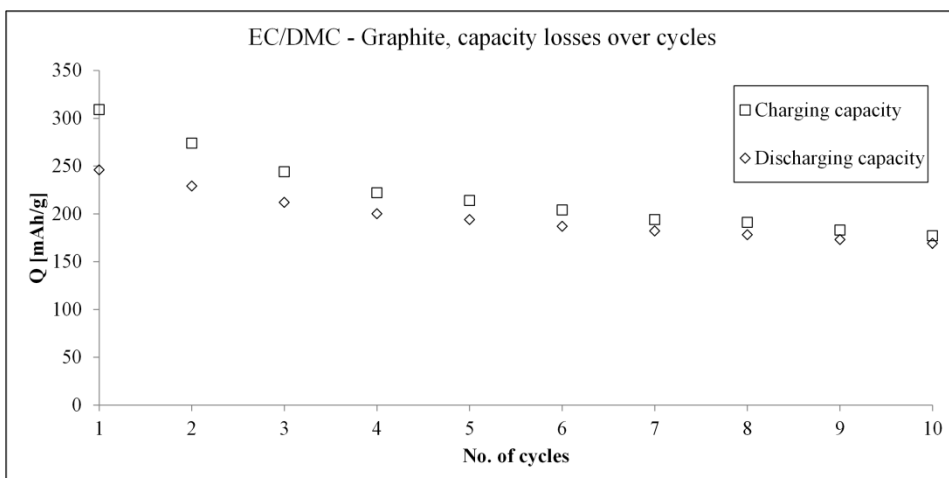


Fig. 2. Capacity development during 10 charge-discharge cycles of natural graphite in EC/DMC solvents mixture

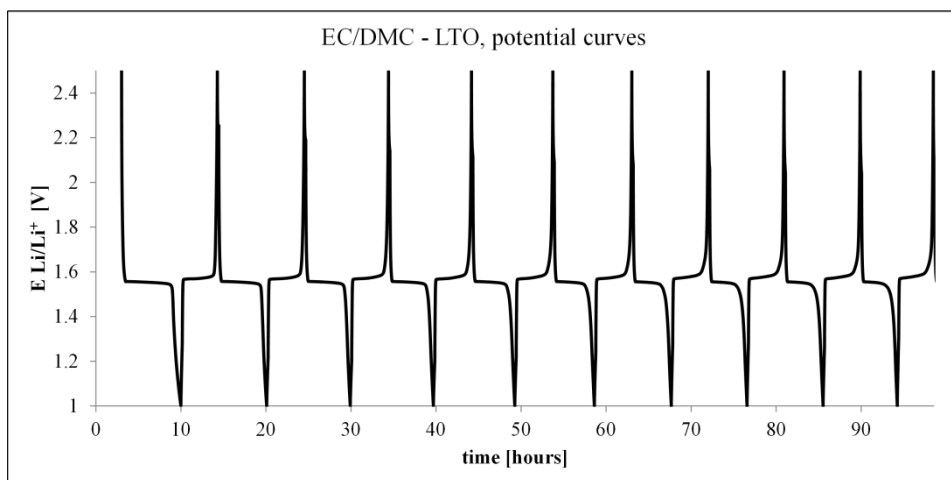


Fig. 3. LTO Charge-discharge characteristics in EC/DMC solvents mixture

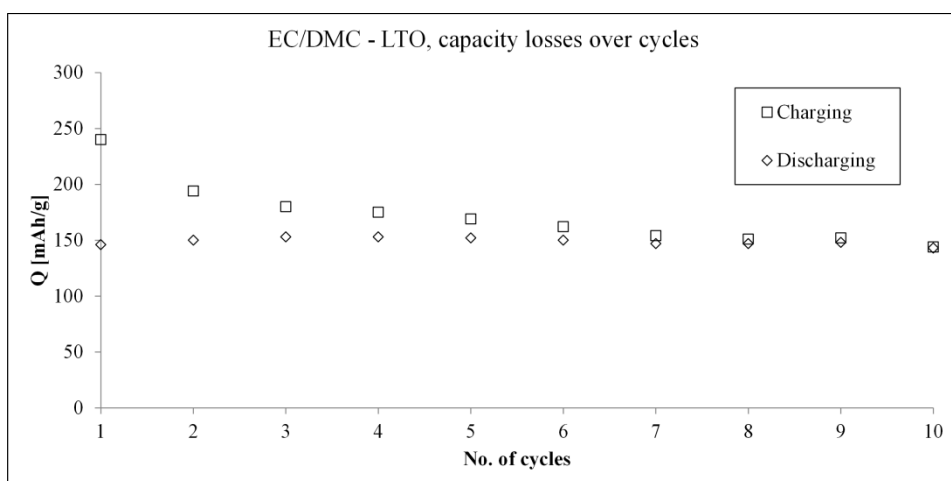


Fig. 4. Capacity development of LTO material during 10 charge-discharge cycles in EC/DMC solvents mixture

All measurements were performed in an electrochemical half-cell set, at three electrode connection. Counter and reference electrode were represented by metal lithium. Electrode specimens were subjected to galvanostatic method measurements which provided capacity characteristics of investigated material. Among the evaluated parameters were stable capacity, irreversible capacity (its origin can be counted to Solid-Electrolyte Interface (SEI) formation) and coulombic efficiency. Fig. 1 shows charge-discharge characteristic of natural graphite; material was cycled in potential window from 50 mV to 2.5 V. In Fig. 4, and Fig. 8 is clearly seen the difference of capacity stability, particularly in case of natural graphite with EC/DMC and sulfolane mixture.

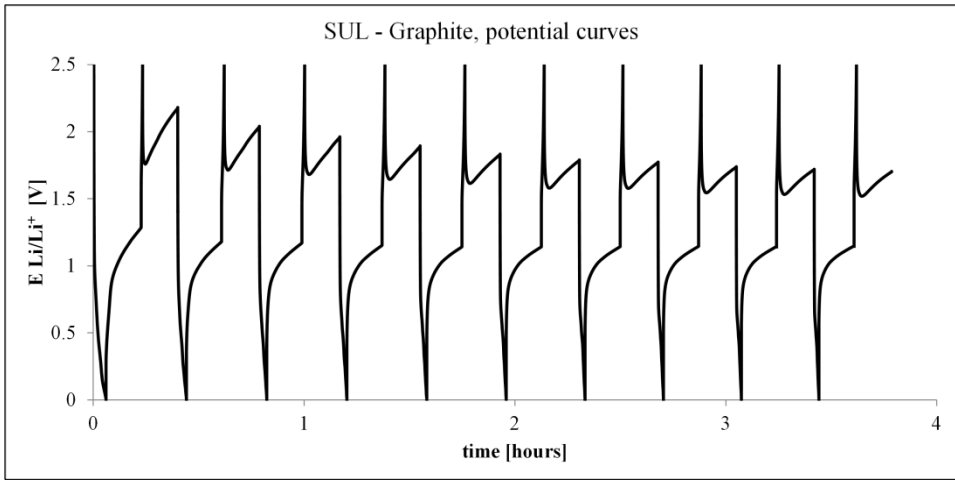


Fig. 5. Potential charge-discharge curves of natural graphite CR5995 in SUL solvent

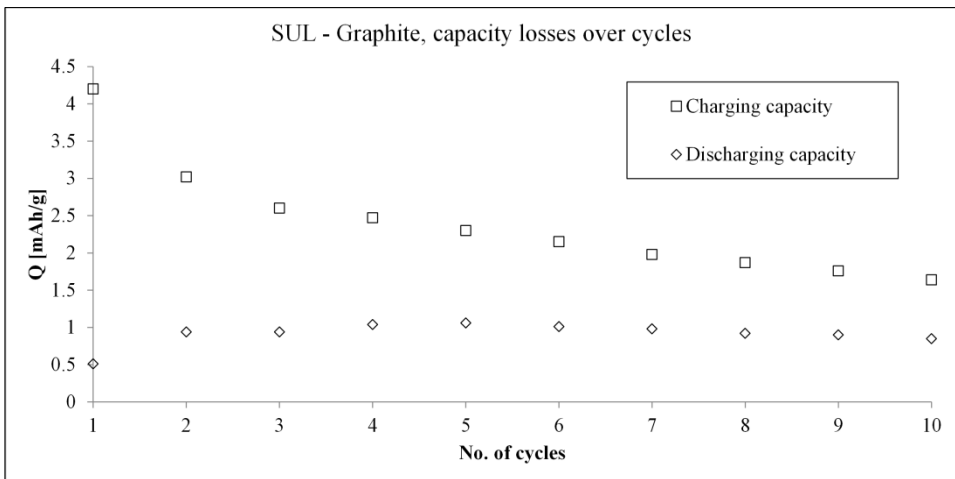


Fig. 6. Natural graphite capacity development during 10 charge-discharge cycles in SUL solvent

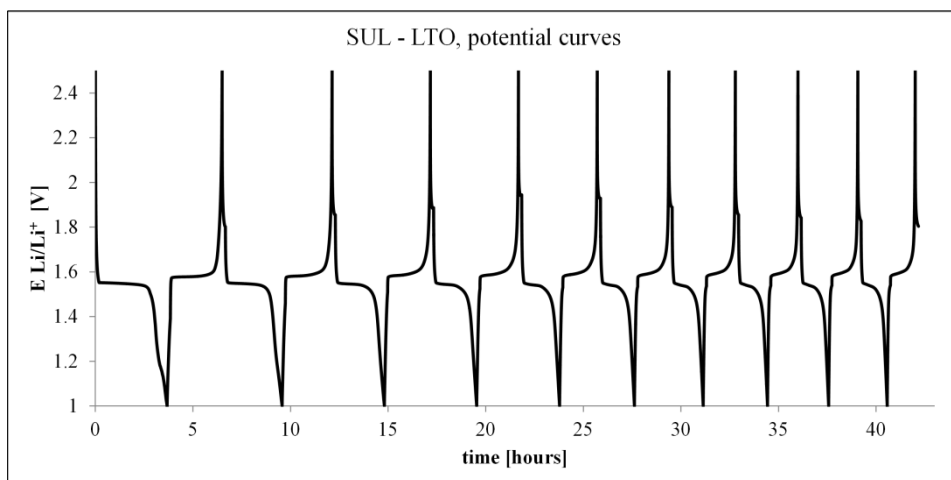


Fig. 7. LTO material, 10 potential charge-discharge curves in SUL solvent

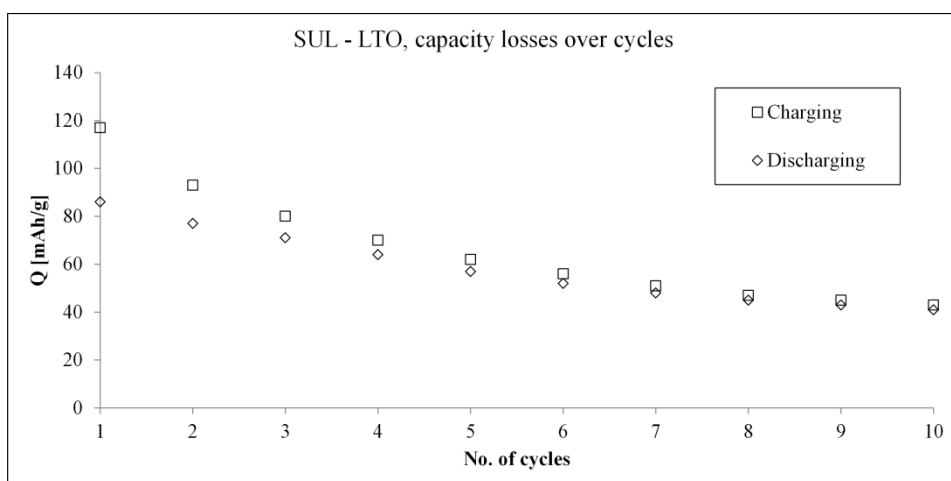


Fig. 8. LTO and sulfolane, capacity development during 10 cycles

Values obtained in experiments are summarized in Tab. 1 below. Tab. 1 shows three main evaluated parameters as stable reversible capacity, irreversible capacity and coulombic efficiency.

Tab. 1 Summary of obtained results

			Cycle No.									
			1	2	3	4	5	6	7	8	9	10
EC/DMC	Dicharg. Capacity [mAh/g]	LTO	240	194	180	175	169	162	154	151	152	144
		Graph.	309	274	244	222	214	204	194	191	183	177
	Irrever. capacity [%]	LTO	18	25	26	38	30	35	40	31	27	22
		Graph.	20	16	13	10	9	8	6	7	5	5
	Coulom. Efficien. [%]	LTO	82	75	74	62	70	65	60	69	73	78
		Graph.	80	84	87	90	91	92	94	93	95	95
SUL	Dicharg. Capacity [mAh/g]	LTO	136	109	87	80	71	63	57	52	48	45
		Graph.	4.2	3.0	2.6	2.5	2.3	2.2	2.0	1.9	1.8	1.6
	Irrever. capacity [%]	LTO	21	15	10	10	8	0	0	0	0	0
		Graph.	88	69	64	58	54	53	51	51	49	48
	Coulom. Efficien. [%]	LTO	79	85	90	90	92	100	100	100	100	100
		Graph.	12	31	36	42	46	47	49	49	51	52

3. Results and discussion

The graphs presented in Figures 1 and 3 show significant differences between potential window and working potential called ‘plateau’ of individual electrode materials. Figure 1 presents the cycling curves of natural graphite with working potential around 0.2 V. On the other hand, Figure 3 shows the LTO material and its working plateau lying around 1.5 V. The working potential of electrode differences puts the LTO material at a little less disadvantage in comparison with graphite. All obtained results are summarised and compared in Table 1 above. They clearly demonstrate that LTO material works with both electrolytes, against it, the graphite is exfoliated by sulfolane. This LTO disadvantage can be suppressed by using high-voltage 5 V positive electrode materials. Among advantages of LTO belong the small irreversible capacity losses that occur during the first two charge-discharge cycles. Figures 2, 4, 6 and 8 show the development of stable reversible capacity. The behaviour of sulfolane with graphite was observed, and exfoliation during contact of graphite that leads to losing of almost overall material capacity occurred. In case of LTO there was observed similar behaviour as presented in Figures 7 and 5. Generally, the LTO material can be considered as a perspective material for a new generation of lithium-ion batteries.

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