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The Influence of Polymer Binders on the Performance of Cathodes for Lithium-Ion Batteries

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Abstract: **A systematic electrochemical investigation is performed to study the effect of polyvinylidene difluoride (PVDF) based polymer binders on the performance of different cathodes for lithium-ion batteries in ionic liquid (IL) based electrolytes. Electrochemical tests indicate that the nature of PVDF effects significantly on cathode stability in IL based electrolytes. The copolymer such as hexafluoropropylene (HFP) plays a significant role in the interfacial resistance. Application of PVDF-HFP binder leads to more cohesive particle network that result in reducing capacity fading of cathodes during the battery cycling.**

Keywords: **polymer binders; cathode materials; lithium-ion battery; ionic liquid**

I INTRODUCTION

The batteries most commonly used in existing cellular phones, personal computers and other electronic devices are lithium-ion batteries (LIBs). Ionic liquids (ILs) are known to be non-volatile, non-flammable and highly conductive. Therefore, an interest has increased recently for possibility of using some ILs in energy storage devices, especially for developing a truly safe lithium-ion battery with a good charge and discharge performance at a middle current density. LIBs principle based on the intercalation-deintercalation of lithium ions in an electrolyte between two battery electrodes (anode and cathode) and corresponding electron stream in an external circuit. In the charged state lithium ions are stored in the anode, which is often based on graphite or carbon material. During LIBs discharge the ions move to the cathode, which is often based on lithium composite oxides. It is recognized [1-3] that the capacity of lithium-ion battery is limited by the cathode capacity. For instance, the initial capacity of graphite anode for LIBs is as minimum 300 mA·h/g (with small irreversible capacity less than 10%). This value is much higher than capacities obtained from conventional cathodes such as $LiCoO_2$ and $LiMn_2O_4$, which are ca 140 mA·h/g. Thus, for further increasing and stabilizing the LIBs capacity it is necessary to develop new effective cathode materials and polymer binders.

In LIBs fabrication process a polymer binder is a material that is very important for binding the active materials of the electrodes. The adhesive and chemical properties of the binder have a great impact on the performance of the battery, especially on the battery serviceability. Usually, a combination of polyvinylidene fluoride (PVDF) and N- methylpyrrolidine (NMP) is used for the binder and the solvent, accordingly. PVDF is soluble in NMP and allows the preparation of slurry having a proper viscosity. Furthermore, PVDF shows a good chemical resistance in a common carbonate-based organic solvents (EC, DEC, DMC) used as electrolytic solution for LIBs. However, PVDF does not meet completely to all of the binder properties required for LIBs, especially for ionic liquid based electrolytes. The active mass can break away from the current collector because PVDF tends to swelling in ionic liquids. Such delaminating process of the active mass leads to declining the performance of LIBs during the process of charging-discharging, quick capacity fading and decreasing the battery serviceability. For this reason it is very important to select a binder, which will reduce the delaminating the active mass. The further improvement of PVDF binder is possible by combination of initial vinylidene fluoride with a copolymer such as hexafluoropropylene (HFP). The presence of copolymer in PVDF binder provides the improved properties for electrode binder, such as adhesion strength and flexibility.

II EXPERIMENTAL

A Preparation of electrodes

The cathode active materials were mixed with 5 wt% PVDF based binder in NMP solution. In the current work two following types of polymer binder were investigated: (I) PVDF, Kynar Flex 2801; (II) NMP- predissolved PVDF-HFP binder (grade KF#9306, available from KUREHA, Advanced Materials Div., Tokyo, Japan). Electrochemical behavior of different cathode materials like $LiCoO_2$, $LiMn_2O_4$, $LiFePO_4$ and $Li_4Ti_5O_{12}$ (which were received mainly from Sud-Chemie, Germany) was investigated in this paper. The mixture was agitated by using a high shear mixer. The resulting slurry was cast onto a metal foil (0.02 mm thick). Doctor blade with a gap opening of 100-200 µm was used to define the maximum thickness of the freshly coated layer. The resulting film was dried at $120^{O}C$ under air flow in order to evaporate the NMP. In some cases the electrodes were compacted to the desired density by calendaring. After compaction, the electrodes were dried again under a primary vacuum at $120^{O}C$ in the time frame of 12 hours. The active loading of the cathode was in the range of 1-20 $mg \cdot cm^{-2}$. The thickness of the electrodes was monitored with a Mitutoyo micrometer (Japan). The thicknesses of the electrodes have varied in the range of 0.02-0.10 mm.

B Electrochemical characterization

The disc electrodes having the diameter of 16 mm, were cut out of the coated film cast onto metal foil current collector using a punch. The 2016 coin lithium-ion cells (the diameter of 20 mm and the thicknesses of 1.6 mm) were assembled in the argon filled glove box (Unilab model, MBraun, USA). The following procedure was employed: (i) electrode was placed

in a bottom can; (ii) TEKLON™ EDEX separator (manufactured by ENTEK Membranes LLC, USA) with the diameter of 19.5 mm was placed on the face of electrode and affixed to it by a polypropylene ring gasket; (iii) electrolyte was spread on a top of separator; (iv) SS grid (ca 14 mm diameter) was welded to the top cap of the cell. After that the 16 mm diameter Li disk was placed on the SS grid of the cap. In the case of a full lithium-ion cell mockup the SS spring was placed in a cell cap (the spring was not used in the case of a "half-cell", where Li foil counter electrode was used); (v) coin cell was compressed and sealed using a coin-cell crimping device.

Electrochemical investigations were performed using the battery cycler MSTAT 32 from Arbin Instruments (USA) and the multi-channel potentiostat/galvanostat VMP3 from Princeton Applied Research (UK).

III RESULTS AND DISCUSSION

In this work electrochemical behavior of different cathode materials like $LiCoO_2$, $LiMn_2O_4$, $LiFePO_4$ and $Li_4Ti_5O_{12}$ was comparatively investigated in the 1M $LiPF_6$ in EC:DEC:DMC=1:1:1 w/w electrolyte (so called LP71 conventional electrolyte - #1), as well as in the electrolytes based on the following ILs from ENEA (Rome/Casaccia, Italy): N-methyl-N-propyl pyrrolidinium bis(fluorosulfonyl)imide (PYR13FSI) - #2 and N-methyl-N-buthylpyrrolidinium bis(trifluoromethansulfonyl)imide (PYR14TFSI) - #3.

2016 coin cells were assembled to evaluate the electrochemical performance of different cathode materials. The coin cells were cycled by applying a constant current in the range from C/20 to C. A minimum of three cells were used for each test condition.

A comparison testing the PVDF and PVDF-HFT based cathodes in different electrolytes indicates considerable decreasing stability of electrodes in IL based electrolytes. For example, the cycling properties of $LiCoO_2$ electrode, based on both types of binders, plotted in Fig. 1.

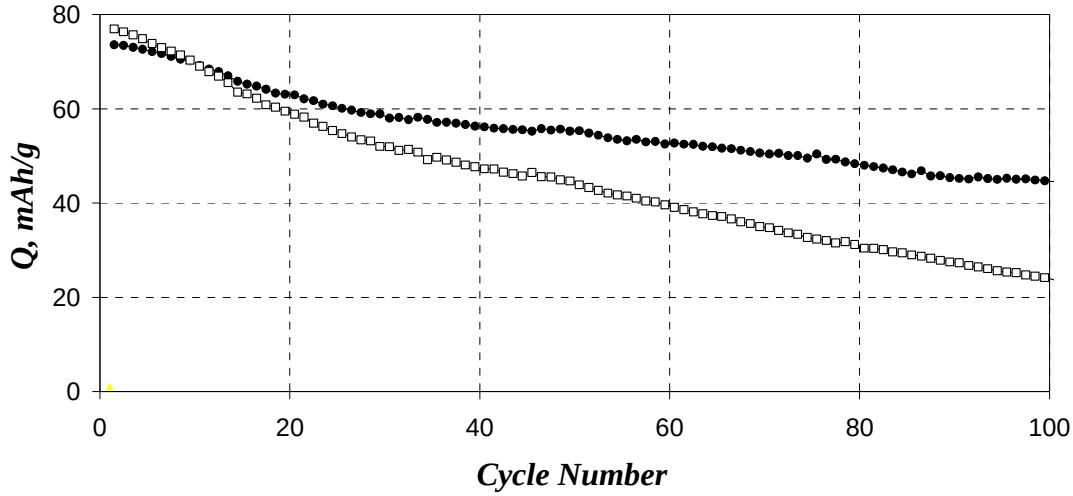

Fig. 1: The cycling properties of $LiCoO_2$ electrode prepared using PVDF (□-line) and PVDF-HFT (●-line) as a binder. Electrolyte - Pyr14TFSI

TABLE 1

THE CAPACITY OF CATHODE MATERIALS AT DIFFERENT ELECTROLYTES AND DISCHARGE MODES

MATERIALS	ELECTROLYTE	$Q_{REVERSIBLE}$ AT DIFFERENT DISCHARGE RATE, MA·H/G			
		C/10	C/5	C/2	C
$LiMn_2O_4$ (EXM1663)	LP71	90	89	87	82
	IL	51	34	22	10
	IL+LP71	67	58	43	31
$LiCoO_2$ (EXM 1058)	LP71	127	112	105	93
	IL	74	62	43	27
	IL+LP71	94	78	66	55
$Li_4Ti_5O_{12}$ (EXM 1037)	LP71	135	133	123	119
	IL	97	82	73	58
	IL+LP71	128	116	95	82
$LiFePO_4$ (EXM 1195)	LP71	149	147	141	139
	IL	83	72	53	38
	IL+LP71	107	84	75	69

The reason of this phenomenon is assumed to be swelling the PVDF in ionic liquids. However, there is some difference in the rate of decreasing. With PVDF binder a capacity decreases and becomes of about 30% of initial capacity after 100 cycles. With PVDF-HFP binder a capacity decreases also but demonstrates of about 60% of initial value after 100 cycles. These results show that using the PVDF-HFP binder leads probably to more stable contact of active material with a current collector. Therefore, the HFP copolymer promotes to formation of more stable electrodes. The data for testing different PVDF-HFP based cathodes in different electrolytes and modes are summarized in the Tables 1. The value of specific capacity depends very strongly on the type of electrolyte (LP71, IL or their mixture IL+LP71).

It is important to understand the factors governing the capacities of cathodes based on $LiCoO_2$, $LiMn_2O_4$, $LiFePO_4$ or $Li_4Ti_5O_{12}$ in order to use full advantages of these materials.

We have established that the voltage profiles of electrodes based on $LiCoO_2$, $LiMn_2O_4$, $LiFePO_4$ and $Li_4Ti_5O_{12}$ in the electrolytes #2 and 3 were quite smooth and almost identical to that for a conventional electrolyte #1). On the other hand, an essentially smaller capacity of cathode materials was observed in the IL based electrolytes.

We have proposed to use a mixture of ILs with common organic electrolytes to improve a capacity and cycling properties of cathodes in ILs based systems. Figs. 2 and 3 show the initial charge/discharge curves for the cells containing Pyr_{14}–TFSI and Pyr_{14}–TFSI with 5% of organic electrolyte LP71 (Pyr_{14}–TFSI-LP71), respectively.

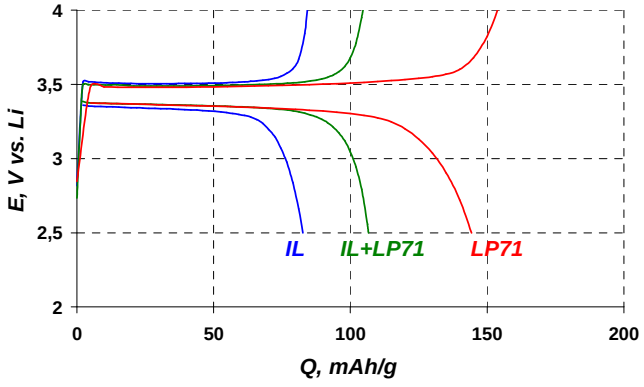

Fig. 2: Electrochemical charge/discharge characteristics of $LiFePO_4$ electrode. Electrolyte: **LP71**- 1M $LiPF_6$ in EC:DEC:DMC; **IL+LP71**- 0.3MLiTFSI PYR_{14}TFSI containing 5 % of 1M $LiPF_6$ in EC:DEC:DMC; **IL** - 0.3MLiTFSI PYR_{14}TFSI

We suggest that IL viscosity is somehow related with lithium diffusion within the composite cathode because lithium diffusion determines the current rate. The capacity dependence on current rate is similar for cells using $LiCoO_2$, $LiMn_2O_4$ and $Li_4Ti_5O_{12}$ cathodes. This is probably because a liquid electrolyte does not penetrate enough into the PVDF film covering the cathode particles during the period of the experiment, and, hence, limiting the oxide accessibility for charging and discharging. For the carbon coated $LiFePO_4$ based cell IL electrolyte may penetrate into cathodes relatively fast, perhaps because the carbon shell or PVDF film covering the particles is thinner. The discharge capacity of cathode material seems depends on the amount of IL based electrolyte inside of electrode. In other words, higher electrolyte content in the bulk of electrode provides higher capacity. Also the columbic efficiency and cycling life seems to depend on the electrolyte component. The cycling properties of $LiFePO_4$ electrode, for example, plotted in Fig. 4

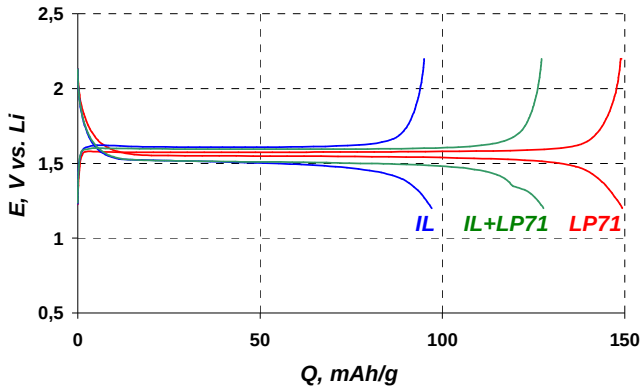

Fig. 3: Electrochemical charge/discharge characteristics of $Li_4Ti_5O_{12}$. Electrolyte: **LP71**- 1M $LiPF_6$ in EC:DEC:DMC; **IL+LP71**- 0.3MLiTFSI PYR_{14}TFSI containing 5 % of 1M $LiPF_6$ in EC:DEC:DMC; **IL** - 0.3MLiTFSI PYR_{14}TFSI

Cycling behavior of cells with Pyr_{14}–TFSI-LP71 was better than that with Pyr_{14}–TFSI, corresponding to variation of capacity for the cells during the cycling. During the period of initial 80 cycles the capacities keep a slow increasing with the cycle number. This is probably because the electrodes have not been completely wetted by Pyr_{14}–TFSI-LP71 electrolyte. With cycling, the liquid electrolyte penetrates into the porous electrodes to promote ionic conduction in the electrodes. As a result, capacity of the cell is increased. After achieving the maximum capacity (140 $mA{\cdot}h{\cdot}g^{-1}$) the cell remains reversible for cycling with very good capacity retention. Thus, IL based electrolyte containing the small amount of organic electrolyte (5 %) could demonstrate a satisfactory performance. During the initial cycles discharge capacity gradually increasing, but after 80 cycles specific capacity seems to be almost the constant for the cell with Pyr_{14}–TFSI-LP71 (Δ-line, Fig. 4). After the initial cycling the capacity values of $LiFePO_4$ electrode are slightly lower than that in the conventional organic solvent electrolytes using a similar coin-cell setting. The columbic efficiency was quite close to 100% excepting the few initial cycles, and this indicates the entire electrolyte was stable during the charge–discharge cycles. On the other hand, the capacity of the cell with Pyr_{14}–TFSI decreased gradually and monotonously (□- line, Fig. 4). The Columbic efficiency was low (91–95%). The capacity decay in Pyr_{14}–TFSI could take place due to the degradation of the electrolyte or to the breakdown of Li electrode. Lithium may be considered to be responsible for the decomposition of electrolyte at the lithium counter electrode surface.

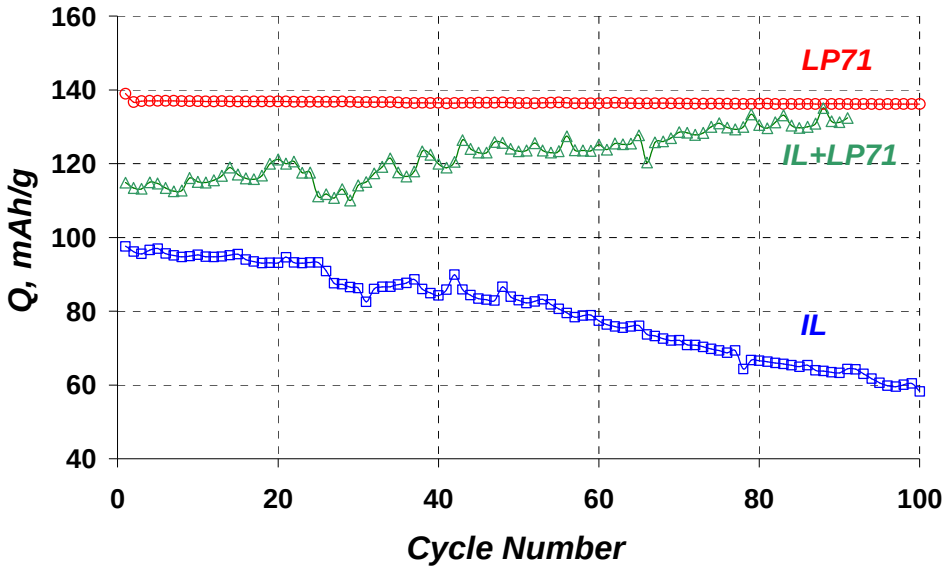

Fig. 4: Discharge capacities of $LiFePO_4$ electrode as a function of cycle number.
Electrolyte: **LP71**- 1M $LiPF_6$ in EC:DEC:DMC; **IL+LP71**- 0.3MLiTFSI $PYR_{14}TFSI$ containing 5 % 1M $LiPF_6$ in EC:DEC:DMC; **IL** - 0.3MLiTFSI $PYR_{14}TFSI$

IV CONCLUSION

The results of current work have shown that using the PVDF–HFP leads to better contact active materials to current collector. Therefore, HPF copolymer makes the formation of more electrochemically stable electrodes in ILs based electrolyte.

Additive even of 5% of organic electrolyte to IL is assumed to provide a sufficient level of $LiFePO_4$ and Li_4Ti5O_{12} electrodes performance. It is possible to conclude from the results obtained that Pyr_{14}–TFSI–LP71 could be a good candidate for IL based electrolyte for lithium-ion battery systems.

Future investigations have to point out for further improving the composition of electrolyte and to develop a more efficient method for filling electrode by electrolyte.

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Vladimirs Homenko, Vjačeslavs Barsukovs. Polimēra saistvielu ietekme uz katodu veiktspēju/efektivitāti litija jonu baterijās.
Darbā izpētīta dažādu katodu materiālu ($LiCoO_2$, Li MnO_4) elektroķīmiskā izturēšanās dažādu elektrolītu šķīdumos (LP71) (N1), tie salīdzināti ar rūpnieciski patreiz izmantotiem elektrolītiem, kas veidoti uz N-metil N-propilpirrolidīna bis-fluorosulfonilimīda (PYR 13 FSI) (N2) un n-metil-n-butilpirrolidīna bis(trifluorometilēnsulfonil)imīda (PYR14 TFSI) (N3) bāzes. Lai novērtētu pētīto materiālu elektroķīmisko uzvedību, izmantoti dažādi katodu materiāli. Tiem novēro dažādu stabilitāti dažādos elektrolītu šķīdumos, katoda materiāli arī daļēji uzbriest elektrolītos. Tas ir ļoti svarīgi, jo lielā mērā nosaka pārklāto katodu kapacitāti. Līdzīgu ainu novēro arī elektrolīta N2 gadījumā. Turklāt jāpiezīmē, ka no elektrolītiem veidojas arī dažādi pārklājumu biezumi un dažāds elektrolīta penetrēšanās dziļums katodos. Veikti arī sistemātiski elektroķīmiskie pētījumi par polivinilidēna difluorīda (PVDF) bāzētu polimēru saistvielu ietekmi uz dažādu katodu veiktspēju litija jonu baterijās jonu šķidrumu (JŠ) bāzētos elektrolītos. Elektroķīmiskie testi norāda, ka PVDF daba būtiski ietekmē katoda stabilitāti JŠ bāzētos elektrolītos. Tāds kopolimērs kā heksafluorpropilēns (HFP) spēlē nozīmīgu lomu uz starpfāžu pretestību. PVDF-HFP saistvielas izmantošana nodrošina labāku daļiņu saistīšanos sistēmā, kā rezultātā bateriju ciklizēšanas procesā notiek katodu kapacitātes zudumi. Nākotnes pētījumos paredzēts vēl vairāk uzlabot elektrolītu piedevu efektivitāti tās sašujot, kā rezultātā palielināsies bateriju kalpošanas ilgums.

Володимир Хоменко, Вячеслав Барсуков. Влияние полимерных связующих на работоспособность катодов литий-ионных батарей.

В работе исследовано электрохимическое поведение различных катодных материалов в различных растворах электролитов (ИП. ЛП71) (N 1) и сравнено с электролитами применямыми в промышленности которые в настоящее время получены из N-метил- N-пропилпирролидина бис-флуоросулфонилимида (PYR13FSI) (N2) и N - метил - N -бутилпирролидина бис(трифлуорометиленсулфонил)имида (PYR14 TFSI) (N3). Для различных катодных материалов наблюдается различная стабильность в различных растворах электролитов. Катодные материалы частично набухают в электролите (N 1). Это важно поскольку набухание в большой мере определяет электрическую емкость катода. Схожее поведение катода наблюдается при его выдержке в элетролите N 2. Выполнены также систематические электрохимические исследования по изучению влияния полимерных связующих на основе поливинилиденфторида (ПВДФ) на работоспособность различных катодов литий-ионных батарей в электролитах на основе ионных жидкостей. Электрохимические испытания показали, что природа ПВДФ значительно влияет на стабильность катода в электролитах на основе ионных жидкостей. Такой со-полимер как гексафторпропилен (ГФП) оказывает значительное влияние на межфазное сопротивление. Использование ПВДФ-ГФП связующего приводит к лучшему сцеплению частиц в системе, что находит проявление в уменьшении степени снижения емкости катодов в процессе циклирования батареи. В дальнейших исследованиях намечаются работы способствующие приросту срока службы литиевых батарей.