CONDUCTIVITY OF LITHIUM PERCHLORATE SALT DISSOLVED IN DIFFERENT TYPES OF SOLVENT.

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Abstract: Lithium perchlorate ($LiClO_4$) is usable crystalline salt for electrolyte in a rechargeable lithium ion battery (LIB). $LiClO_4$ is an inorganic compound with white color. In the present study the conductivity and the electrochemical behavior of electrolytes based on $LiClO_4$ was examined by using impedance spectroscopy (EIS) and linear voltametry (LSV) measurement at a room temperature. The resistance (conductivity) of electrolytes with different molar concentration of $LiClO_4$ dissolved in different types of the solvent was measured in the first part of this work. In the second part electrochemical behavior of two electrolytes with the highest conductivity was measured and evaluated by using a potential window. At the end the sodium perchlorate $NaClO_4$ (for NIBs) was measured in this study too.

Keywords: Lithium perchlorate, $LiClO_4$, Sodium perchlorate, $NaClO_4$, Electrolyte, Li-ion battery

1 INTRODUCTION

"Li-ion batteries are one of the most successes of modern electrochemistry. These batteries, which became a commercial reality about a decade ago, are conquering the markets with increasingly wider applications. Present challenges are to extend their use to high power and large size applications (e.g., propulsion, EV). The current systems use graphitic carbons as the anode material, LiCoO2 as the major cathode materials, mixtures of alkyl carbonates including ethylene carbonate (a mandatory component for sufficient negative electrode passivation), dimethyl, diethyl, and ethylmethyl carbonates (EC, DMC, DEC, EMC, respectively), and LiPF6 as the electrolyte solution. The alkyl carbonates were chosen due to their acceptable anodic stability for the 4 V cathodes used in Li-ion batteries, as well as lithiated graphite, together with other properties, such as high polarity (i.e., good conductivity of their solutions), a reasonable temperature range between freezing and boiling points, sufficiently low toxicity, and accept able safety features. The LiPF6 salt is, to some extent, also a compromise" [1].

"A lithium ion accumulator directly converts electrical energy and chemical energy reversibly by use of lithium ions in a chemical redox reaction. However, with respect to the high energy density in lithium ion cells, there are still challenges regarding safety, high voltage applications, and long-term stability. Therefore, a broad research on electrolytes, cathode, and anode materials is performed from numerous scientific groups and companies. Major interest lies in the study of additives to the electrolytes which are applied for a specific and selective purpose. Numerous classes of different compounds are already identified which result in highly selective effects in a Li-ion based cell [2].

In this study a series of six aprotic solvents in a liquid electrolyte mixture based on $LiClO_4$ salt (for LIBs) were studied with respect to the usability in Li-ion cells. Namely, Propylene carbonate (PC), Dimethylformamide (DMF), Diethoxyethane (DEE), Dimethoxyethane (DMC), Ethylene carbonate (EC), Dimethyl carbonate (DMC) and Diethyl carbonate (DEC). This salt ($LiClO_4$) instead of ($LiPF_6$) was chosen because I am looking for the eqvivalent liquid electrolyte to $NaClO_4$ (for

NIBs)- Genrally, sodium perchlorate is well soluble in many organic solvents. It the next study will be examinated differences in the intercalation and deintercalation process into the graphite structure used in sodium + graphite system and lithium + graphite system. I have the experience that the other usable salt for NIBs electrolyte like a $NaBF_4$ and $NaPF_6$ are so bad soluble under the conditions known for us.

2 EXPERIMENTAL PART

2.1 MEASURING WORKSTATION AND METHODS

For the experimental part a lithium perchlorate ($LiClO_4$) and a sodium perchlorate ($NaClO_4$) salt from company Sigma Aldrich (used as received) were selected. The main electrolyte parameters (conductivity of electrolyte and electrochemical stability) were examined. Experiments were carried out in AtmosBag (Sigma Aldrich). On the field of liquid electrolytes was examining behavior of aprotic electrolytes which were prepared from the suitable salt which was dissolved in organic solvent (see table 1). Electrochemical measurements were made on the station BioLogic VMP3 and the results were evaluated by calculation software EC-Lab V10.39. Parameters of measuring methods (see table 2).

Solvent	Salt
Diethoxyethane	$LiClO_4$
Dimethoxyethane	
Dimethylformamide	
Ethylene carbonate + Diethyl carbonate; 1:1 weight ratio	
Ethylene carbonate + Dimethyl carbonate; 1:1 weight ratio	
Propylene carbonate	

Table 1: List of solvents and salt used.

For the measurement of conductivity was used commercial conductivity cell KC 503 from company THETA ’90. On the beginning the salt $LiClO_4$ was weighed on the laboratory digital weight and put in to the small glass vials. After that, appropriate amount of specific solvent was added. For the mixing was used electromagnetic stirrer. At the end of this process were prepared 4 ml solutions from all types of solvent with $LiClO_4$ and two types with $NaClO_4$ (see table 4) salt in molar concentrations 0.1 ; 0.25 ; 0.5 ; 0.75 ; 1.00 and 1.25 mol/l (see table 3).

EIS	LSV
U_{ss} = 0 V	U_{begin} = 0 V
U_a = 5 mV	U_{end} = 3,5 V
f = 100 kHz – 100 Hz	α =0.5 mV/s
Note .: potential U_{ss}, U_{begin}, U_{end} measured against counter electrode	

Table 2: Parameters of the measuring methods EIS and LSV.

2.2 DISCUSSION OF MEASURED AND CALCULATED DATA

Electric conductivity and potential window were measured. It is possible to see that the highest electric conductivity is globally somewhere in the interval from 0.75 to 1.25 M concentration for all solvents. The best electric conductivity was achieved by DMF solvent, exactly 1.25 M $LiClO_4$ dissolved in DMF. The second best electric conductivity by 1 M $LiClO_4$ electrolyte dissolved in EC/DMC 1:1 weight ratio (see table 3 and picture 1) was measured. The conductivity of $NaClO_4$ liquid electrolyte (see table 4 and picture 2) is similar with the $LiClO_4$ liquid electrolyte.

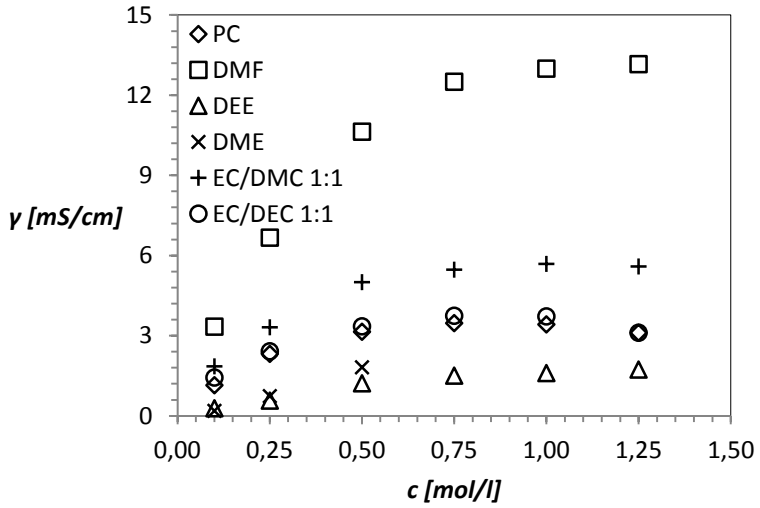
$LiClO_4$	γ [mS/cm]					
c [mol/l]	0.10	0.25	0.50	0.75	1.00	1.25
PC	1.14	2.32	3.14	3.47	3.42	3.11
DMF	3.33	6.67	10.64	12.50	12.99	13.16
DEE	0.29	0.57	1.21	1.51	1.60	1.73
DME	0.18	0.73	1.82	N[1)]	N[1)]	N[1)]
EC/DMC 1:1 hm.	1.86	3.31	5.00	5.46	5.68	5.59
EC/DEC 1:1 hm.	1.44	2.41	3.34	3.75	3.72	3.11

1) Salt of this concentration is not dissolve.

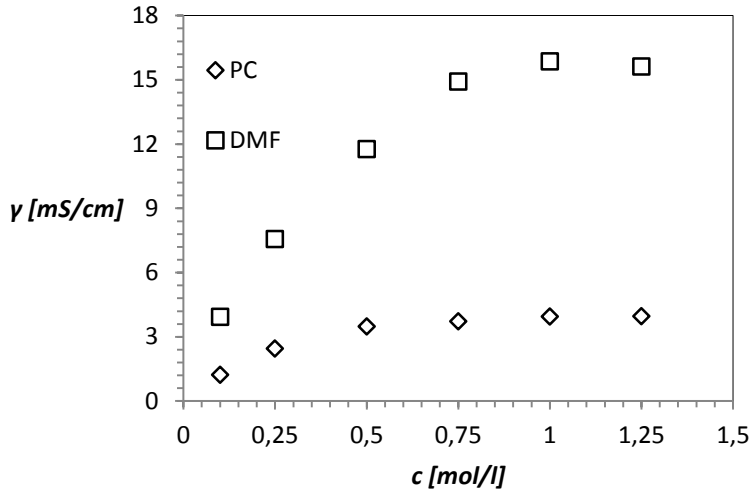
Table 3: Conductivity of liquid electrolytes.

$NaClO_4$	γ [mS/cm]					
c [mol/l]	0.10	0.25	0.50	0.75	1.00	1.25
PC	1.24	2.46	3.50	3.37	3.95	3.97
DMF	3.94	7.58	11.76	14.93	15.87	15.63

Table 4: Conductivity of liquid electrolytes.



Picture 1: Liquid electrolytes conductivity depending on $LiClO_4$ concentration.



Picture 2: Liquid electrolytes conductivity depending on $NaClO_4$ concentration.

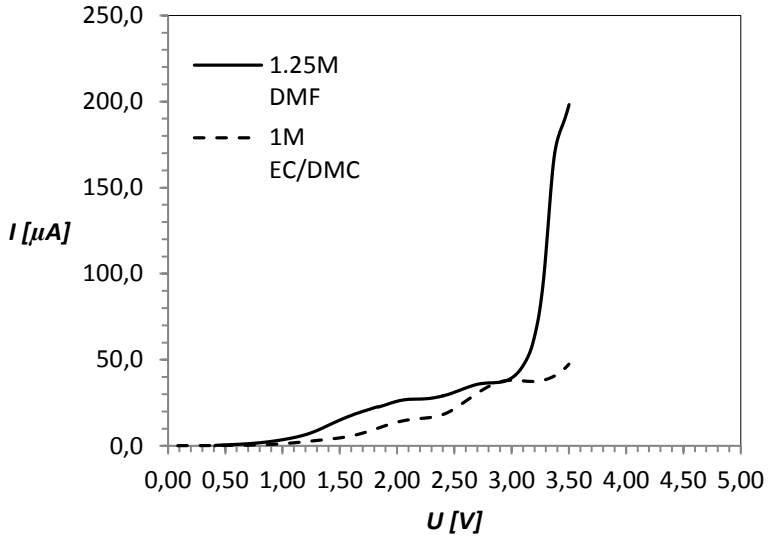
2.3 POTENTIAL WINDOW

For these experiment were mixtured 1.25 M $LiClO_4$/DMF electrolyte and 1 M $LiClO_4$/EC/DMC 1:1 weight ratio electrolyte according to table 3. Experiment was measured in the ECC-ESD cell in AtmosBag with the argon atmosphere. It was 2-electrode measurement with the working electrode and counter electrode bouth made of steel. In to this ECC-ESD cell was put in the glass fibre separator (type: Z-4, Papírna Perštejn s.r.o.) and was droped in 100 µl of electrolyte by the pipette. The LSV curves you can see on picture 3 and the potential for I_{max} = 5µA (see table 5).

	$LiClO_4$
	U [V]
1.25 M DMF	1.11
1 M EC/DMC 1:1 weight ratio	1.54
	U_{cell} [V]
1.25 M DMF	2.22
1 M EC/DMC 1:1 weight ratio	3.08

Note.: potential U was measured for Imax = 5µA

Table 5: Decomposition potential of electrolytes.



Picture 3: LSV of two chosen electrolytes with highest conductivity.

3 CONCLUSION

The best conductivity 13.16 mS/cm was measured by 1.25 M $LiClO_4$/DMF electrolyte. All concentration of $LiClO_4$ dissolved in DMF aprotic solvent are much more conductive than others electrolytes with the same salt but different type of solvent. However, there can be suspiction to presence of the H_2O particles in DMF solvent. This can be the reason why is possible to see some cureent flow at low potential (1V) on LSV curve of 1.25 M $LiClO_4$/DMF electrolyte . It will be the subject of the next examination. Further will be proven that the reversible cycling 1.25 M $LiClO_4$/DMF electrolyte with commercially available active materials is possible or isn't.

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