

# Improving the interfacial resistance in lithium cells with additives

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## Abstract

Improved interfacial resistance was observed in lithium cells by the use of new additives. The additives, nitrile sucrose and nitrile cellulose and their lithium salts, were evaluated in polyvinylidene difluoride (PVDF) thin-film gelled electrolytes containing a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). The electrochemical properties of the films with and without the additives were measured as a function of temperature and compared. The interfacial resistance ( $R_{in}$ ) of the films with the additives was significantly lower than that without the additives, especially at sub-ambient temperatures. For example, the  $R_{in}$  at  $-20^{\circ}\text{C}$  for the films with additives was around  $7000\ \Omega\ \text{cm}^2$  and that for the films without the additives was  $>20,000\ \Omega\ \text{cm}^2$ . Results obtained from using the additives in lithium-ion (Li-ion) cells show significant improvements in the low frequency resistance of the cells. © 2001 Published by Elsevier Science B.V.

**Keywords:** Lithium-ion cells; Electrolyte additives; Interfacial resistances

## 1. Introduction

In recent years rechargeable lithium-ion (Li-ion) batteries (also called “rocking chair”, “shuttlecock” or “swing electrode”) containing either organic liquid electrolytes or gelled electrolytes are being extensively investigated as commercial power sources because they offer higher energy per unit weight and volume than nickel-based batteries such as Ni/Cd or Ni/MH [1]. Further, the self-discharge rate of Li-ion batteries is low — about 2% of capacity per month — compared to 15% for Ni/Cd and 25% for Ni/MH. Because of these potential advantages, Li-ion batteries are being investigated for a number of applications including electric vehicle (EV), space, military and commercial. In commercial Li-ion cells, coke or graphite is used as the anode and  $\text{LiCoO}_2$  is used as the cathode. The specific capacity is  $372\ \text{mAh}\ \text{g}^{-1}$  for the anode and  $\sim 140\ \text{mAh}\ \text{g}^{-1}$  for the cathode. New higher capacity metal-based anodes [2] and mixed-oxide cathode materials (for example  $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ ) [3] are being developed for use in Li-ion batteries to increase the delivered energy in order to meet the ever increasing power demands of the digital revolution. Further, new low temperature electrolytes [4] and shutdown separators are being investigated for extending the low-temperature performance and safety, respectively, of the batteries. However,

in large part, the impedance behavior, which impacts the electrical performance of Li-ion cells, has been overlooked. No thorough and systematic studies have been reported in the literature on the impedance characteristics of Li-ion cells.

We at Sandia National Laboratories have published several papers on the impedance behavior of Li-ion cells [5–7]. Our studies indicate the following.

1. The ohmic resistance of a Li-ion cell remains low and nearly constant between  $-20$  and  $35^{\circ}\text{C}$ .
2. The total cell impedance increases by an order of magnitude at  $-20^{\circ}\text{C}$ .
3. The increase in cell impedance comes mostly from the cathode–electrolyte interface.

Exploring ways to reduce interfacial resistance ( $R_{in}$ ) is paramount since the much-touted benefits of Li-ion cells over Ni/Cd and Ni/MH will not be realized at sub-ambient temperatures. Our impedance studies underscore the importance of a very low interfacial resistance for high power applications. Especially at sub-ambient temperatures (say  $-20^{\circ}\text{C}$ ) the effect of  $R_{in}$  will be much more pronounced than at elevated temperatures. Even the state-of-the-art non-aqueous electrolytes such as propylene carbonate (PC)/diethyl carbonate (DEC) and ethylene carbonate (EC)/dimethyl carbonate (DMC) which are currently being used in the Li-ion commercial cells, show unacceptable  $R_{in}$  values especially at sub-ambient temperatures. In some instances  $R_{in}$  values as high as  $500\ \Omega\ \text{cm}^2$  have been reported [8].

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Primarily, the bulk electrolyte resistance and  $R_{in}$  dictate the deliverable power of the battery. Over the years, many different approaches have been successfully made to improve the bulk ionic conductivity of the electrolyte to  $>10^{-3} \text{ S cm}^{-1}$  at room temperature. For example, one of the approaches involves immobilizing organic liquid electrolytes in an electrochemically inactive host polymer (these are called gelled electrolytes), such as polyacrylonitrile (PAN) [8] and polyvinylidene fluoride (PVDF) [9]. This is commendable since it permits the use of thicker electrolyte films without the inherent problems of pin holes and insufficient mechanical stability that are associated with thinner electrolyte films. However, the  $R_{in}$ , which acts in series with the bulk electrolyte resistance, is not optimized, which severely impedes the realizable power. Further, no studies aimed at reducing the  $R_{in}$  have been reported in the literature.

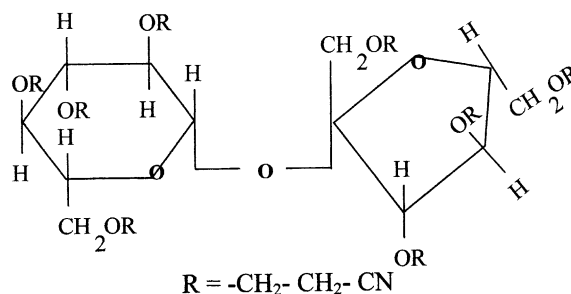
At Sandia National Laboratories we made a systematic attempt to reduce the  $R_{in}$  of the state-of-the-art electrolytes by small quantities of additives. These additives include nitrile sucrose (SUCN) and nitrile cellulose. These are saturated cyclic compounds with functional groups that are known to be stable toward lithium and their lithium salts. These additives are inexpensive, non-hazardous, and stable up to at least  $200^\circ\text{C}$ . More importantly they dissolve in common organic solvents. This paper describes the syntheses of lithium salts of the additives, fabrication of thin film PVDF-based gelled electrolytes with and without the additives, and discusses results of electrochemical studies.

## 2. Experimental

### 2.1. Syntheses of the lithium salts of nitrile sucrose and nitrile cellulose

The precursor chemicals were purchased, respectively, from Polysciences, Inc. and from K&K Rare and Fine Chemicals. Only battery grade chemicals were used in this study. These additives have, respectively, six nitrile-groups and eight nitrile-groups per molecule. The salt  $\text{Li}_4\text{SUCN}$  was formed by putting 1.08 g of SUCN into a 100 ml round bottom two-necked flask within a glove box. To this was added 50 ml of tetrahydrofuran (THF) at room temperature and the mixture was stirred well. The flask was tightly sealed and taken out of the glove box, cooled to  $0^\circ\text{C}$  in an ice bath and 2.8 ml of *n*-butyl lithium was injected through a septum. The solution was stirred for 2 h, the ice bath was removed and again stirred overnight. The solvent was pumped off leaving behind a bright yellow deposit. The flask was taken into the glove box and the yellow powder collected. The composition of the yellow powder was confirmed to be  $\text{Li}_4\text{SUCN}$ . A similar procedure was employed for the syntheses of other lithium salts and the weights of the chemicals were adjusted appropriately.

Structure of nitrile sucrose (general formula:  $(\text{C}_{12}\text{H}_{14}\text{O}_3) \cdot (\text{OCH}_2\text{CH}_2\text{CN})_8$ ), a viscous liquid at room temperature is given.



### 2.2. Preparation of PVDF-gelled electrolyte

The solvents EC, PC, and DEC were purchased from Mitsubishi Chemicals, Japan and the  $\text{LiPF}_6$  was purchased from Hashimoto, Japan.

EC was mixed with DEC (1/1, v/v) or with PC (1/1, v/v) and  $\text{LiPF}_6$  was added to the solution mixture at room temperature at 1 M concentration. The preparation and the composition of PVDF-based gelled films are given below.

An amount of 1 g of PVDF (2801) was dissolved in about 15 ml of methyl ethyl ketone (MEK) at  $\sim 40^\circ\text{C}$  and the solution was cooled to room temperature before adding 2 g of the electrolyte solution. The mixture was vigorously stirred for a couple of hours before either doctor-blading or pouring the entire solution in a Teflon mold. The MEK was allowed to evaporate slowly overnight. The films were vacuum pumped at  $40^\circ\text{C}$  for a day before making electrochemical measurements, to obtain bulk and interfacial properties. A similar procedure was followed for making PVDF-gelled films containing the additives. About 0.1 g of the additive was added to 10 g of the liquid electrolyte and 2 g of this solution was added to 1 g of PVDF already dissolved in MEK.

In the films that contain the lithium salt of the additive, the concentration of  $\text{Li}^+$  is higher than 1 M. In order to make a meaningful comparison of the electrochemical properties the  $\text{Li}^+$  concentration in other films and electrolytes was adjusted appropriately. Electrochemical measurements were made on these films as well as on the liquid electrolytes. A standard Princeton Applied Research electrochemical ac impedance system described elsewhere was used to measure the electrochemical properties.

## 3. Results and discussion

Before we studied these additives in PVDF-based gelled electrolytes we studied them as additives in liquid electrolytes. In this paper we report our findings on the use of these materials as additives in the following.

1. EC + DEC + 1 M LiPF<sub>6</sub>.
2. PVDF-based gelled electrolyte containing the above organic liquid electrolyte.

Results are only given for nitrile sucrose as the cellulose analog gave almost identical results.

For ac measurements, a symmetrical cell was used. The electrolyte was sandwiched between two smooth, freshly cut, lithium foils. Stainless steel (SS) foil was used as current collector [i.e. SS/Li//Electrolyte//Li/SS]. The cell assembly was vacuum sealed in a polyethylene laminated aluminum bag. For dc measurements, the electrolyte was sandwiched between two well-polished SS foils [i.e. SS//Electrolyte//SS] (blocking contact) and the cell assembly was also vacuum-sealed. For the solution studies, similar electrode assemblies were used but were assembled within airtight glass cells.

### 3.1. Ac results

A small amplitude ac signal of  $V_{p-p} = 1$  mV was used over the frequency regime 60 kHz to 0.1 Hz. From the Nyquist plot, both the ohmic and the interfacial charge transfer resistance of the liquid electrolytes and PVDF-based gelled electrolytes with and without the additives were measured and are given in Table 1.

These data indicate that, while the additive does not affect the bulk conductivity, (this is almost the same) the interfacial resistance is significantly reduced. In the case of the liquid electrolyte, the reduction in  $R_{in}$  is  $\sim 33\%$  and in the case of the PVDF-gelled electrolyte the reduction is  $\sim 20\%$ . At lower temperatures, the reduction in  $R_{in}$  by the additive is very significant. For example, at  $-20^\circ\text{C}$  the  $R_{in}$  for the PVDF-based gelled electrolytes with and without additives are 7092 and 20,340  $\Omega\text{ cm}^2$ , respectively — an improvement of  $\sim 66\%$ .

### 3.2. Dc results

A wide potential window is a must for these polymers where they have to be used in conjunction with high voltage cathodes. To evaluate the effect of the additives on the voltage window of the electrolytes we measured the window using dc cyclic voltammetry. The studies were made on PVDF-based gelled films sandwiched between two SS electrodes (blocking contacts). The dc results are given in Table 2.

Table 1  
Conductivity and  $R_{in}$  of the electrolytes with and without additive at room temperature

Electrolyte	$\sigma$ ( $\text{S cm}^{-1}$ )	$R_{in}$ ( $\Omega\text{ cm}^2$ )
EC + PC + LiPF <sub>6</sub>	$2.6 \times 10^{-2}$	189
EC + PC + LiPF <sub>6</sub> + Li <sub>4</sub> SUCN	$2.7 \times 10^{-2}$	125
PVDF + EC + PC + LiPF <sub>6</sub>	$1.7 \times 10^{-3}$	80
PVDF + EC + PC + LiPF <sub>6</sub> + Li <sub>4</sub> SUCN	$1.9 \times 10^{-3}$	60

Table 2

Comparison of dc current flows at 0 and 5 V (vs. Li<sup>+</sup>/Li) for PVDF-gelled films with and without additives at  $-20$ , 25 and  $50^\circ\text{C}$

Temperature ( $^\circ\text{C}$ )	Without additive ( $\mu\text{A cm}^{-2}$ )		With additive ( $\mu\text{A cm}^{-2}$ )	
	At 0 V	At 5 V	At 0 V	At 5 V
$-20$	1.7	0.87	2.2	1.3
25	10.4	4.5	12.5	5.5
50	29.4	6.9	21.5	6.9

The currents are compared at 0 and 5 V versus Li<sup>+</sup>/Li for three different temperatures, for the two films. The current flowing through the cell at the two extreme potentials for the cells is comparable, which suggests that the additives do not alter the potential window of the electrolyte.

## 4. Impedance studies on 18650 lithium coin cells

We have constructed Li-ion coin cells with and without additives in their electrolyte.

The results from impedance measurements on 18650 Li-ion cells clearly indicate that the interfacial resistance dominates the cell impedance, especially at sub-ambient temperatures. While the ohmic resistance remains nearly constant in this temperature ( $-20$  to  $25^\circ\text{C}$ ) range the low frequency resistance, which is mostly the electrode/electrolyte charge transfer resistance, increases by approximately 15 times for the same temperature range.

## 5. Impedance studies on gelled electrolytes

Impedance measurements were made on gelled polymer electrolyte systems. In Table 3 are shown resistance values for the PVDF/EC/PC/LiPF<sub>6</sub> gelled system without the additives. The polymer film was sandwiched between two oxide-free Li electrodes. The low frequency resistance is higher than the ohmic resistance.

Resistance values for films with additives are given in Table 4.

As in results reported earlier in this paper, the performance improvements from the two additives, nitrile sucrose and nitrile cellulose, were similar.

Table 3  
The ohmic and low frequency resistances for PVDF-gelled electrolyte without additives

Temperature ( $^\circ\text{C}$ )	Ohmic resistance ( $\Omega$ )	Low frequency resistance ( $\Omega$ )
25	0.077	5.24
10	0.359	17.69
0	0.434	49.56
$-10$	0.801	170.5
$-20$	1.220	565

Table 4  
Ohmic and low frequency resistances for PVDF-gelled electrolyte with additives

Temperature (°C)	Ohmic resistance ( $\Omega$ )	Low frequency resistance ( $\Omega$ )
25	0.079	3.47
10	0.718	8.75
0	1.041	19.86
–10	1.983	63.5
–20	3.470	197

## 6. Impedance studies on 18650 lithium coin cells

We have constructed Li-ion coin cells with and without additives in their electrolyte.

The results from impedance measurements on 18650 Li-ion cells clearly indicate that the interfacial resistance dominates the cell impedance, especially at sub-ambient temperatures. While the ohmic resistance remains nearly constant in this temperature range (–20 to 25°C) the low frequency resistance, which is mostly the electrode/electrolyte charge transfer resistance, increases by approximately 15 times for the same temperature range.

## 7. Conclusions

We studied the electrochemical properties of EC + PC + LiPF<sub>6</sub> liquid electrolyte and PVDF-based gelled electrolytes with and without additives. We have studied nitrile cellulose and nitrile sucrose and their lithium salts as additives. These additives are off-the-shelf and inexpensive chemicals. They are thermally stable to above the shutdown

temperature of the separators. These additives improved the interfacial properties of the electrolytes contacting metallic lithium and did not affect the bulk properties of the electrolyte. Further, the additives did not alter the voltage window of the electrolytes. The improvement in the interfacial properties by the additives is significant at lower temperatures compared to at room temperature.

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