

# EFFECT OF DIFFERENT CARBONS ON ELECTROCHEMICAL PERFORMANCE OF LiCoO<sub>2</sub> COMPOSITE CATHODES

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## ABSTRACT

Different types of carbon and graphite were used as conductive additives to rise up electrochemical performance of LiCoO<sub>2</sub> based composite electrode cathode. The electrochemical performance of the materials was investigated using electrochemical impedance spectroscopy and charge-discharge cycling. The results showed that discharge capacity, the discharge voltage and especially total internal resistance differs significantly with using different conductive elements. Nowadays, different types of carbon and graphite are still the most used materials for increasing electronic conductivity. It is because of easy preparation, high stability and relatively low price in compare with other possibilities.

## 1. ÚVOD

All conventional electrode materials used for lithium-ion cell cathode suffer from poor electronic conductivity, which is in range of  $10^{-2} - 10^{-9}$  S/cm. Because electrode system of a lithium ion battery has to allow flowing of both lithium ions and electrons it is necessary to add some conductive additives to the mass of electrode active material. Many researchers have discovered different conductive materials for cathode electronic conductivity enhancement.

Not only electronic conductivity but also ionic conductivity influences electrochemical performance of the composite cathode. This can be improved mostly by increasing electrode porosity and thus contact surface between electrolyte solution and active material. This is best way to shorten ion diffusion lengths. Higher specific capacity and especially better high rate performance are achieved by template-synthesized hollow-sphere thin wall particles or nanotubes. But for industrial application are these methods unfortunately too expensive.

## 2. EXPERIMENTAL

### 2.1. MATERIALS

The active LiCoO<sub>2</sub> material with particle size about 8µm was provided by LICO Technology Corporation. Carbons were obtained from different suppliers. SUPER P is a conductive carbon black with high to very high void volume originating from the interstices be-

tween the carbon black due to their complex arrangement and porosity. Super P was obtained from Timcal. COND 2995 is micronised graphite with increased conductivity made by Graphite Týn. EXPANDED GRAPHITE was provided by Bochemie a.s. NANOSORB and GP 3893 are high conductivity carbons made by CABOT Corporation Boston. PVDF and NMP for binding, ethylene carbonate, dimethyl carbonate and  $\text{LiPF}_6$  for electrolyte were obtained from Sigma Aldrich. Except the carbons and graphites no purification of used chemicals was made.

## **2.2. ELECTRODE PREPARATION**

All the provided carbons were boiled in mixture of water and isopropyl alcohol and filtered to wash out possible production process residues (greasiness) and to activate surface. Dried out carbons were mixed with  $\text{LiCoO}_2$  active material and milled in ball mill for 1,5 to reduce possible carbon nuggets and for proper material dispersion. In such obtained mixture poly(vinylidene-floride) (PVDF) as a binder and N-methyl-pyrrolidone (NMP) solvent was added. Final weight ratio of  $\text{LiCoO}_2$ :carbon:PVDF used was 80:10:10.

After overnight stirring on magnetic stirrer the obtained paste was coated on a aluminum foil dried well and pressed by 3500 tons/m<sup>2</sup>. For cell assembly 18 mm diameters round electrodes were cut of the coated foil.

Cathode was evaluated by using EL-CELL ECC-STD electrochemical test half-cell (two electrode cell) for aprotic electrolytes. Test cells were assembled in argon atmosphere filled glove box with oxygen and water contain less than 1,2 ppm. Lithium metal foil as negative electrode and ethylene carbonate:dimethyl carbonate in ratio 1:1 with  $\text{LiPF}_6$  salt as electrolyte was used. Glass microfibre round discs were employed as separator.

## **2.3. INSTRUMENTATION AND MAESUREMENT METHOD**

Two methods for performance investigation were applied: galvanostatic charge-discharge cycling and electrochemical impedance spectroscopy. Both methods were carried out by Biologic instrument system in the test cells mentioned above.

Cells were cycled in the potential window of 2,5V - 4,2V vs. lithium. Values of specific charge was calculated only from mass of the active material  $\text{LiCoO}_2$  and for charge-discharge current calculations was supposed to be 140 mAh/g. There were two cycling capacities used – 0,1C and 0,5C.

Electrochemical impedance spectroscopy frequency range used was 1Mhz to 10mHz with amplitude 10mV.

# **3. RESULTS AND DISCUSSION**

## **3.1. CHARGE-DISCHARGE CYCLING**

Specimens were cycled at first three times by current corresponding to 0,1 supposed hour capacity of material (140mAh/g) and then six times by discharge rate of 0,5 supposed capacity (0,5C). Specific capacity in second cycle and specific capacity loss during next cycling was the fiels of my interest.

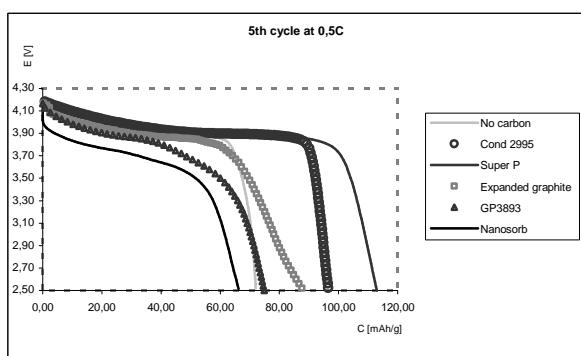


Fig.1 Discharge capacity in 5<sup>th</sup> cycle at rate 0,1C

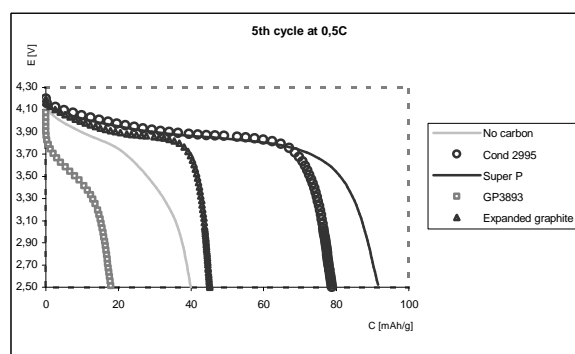
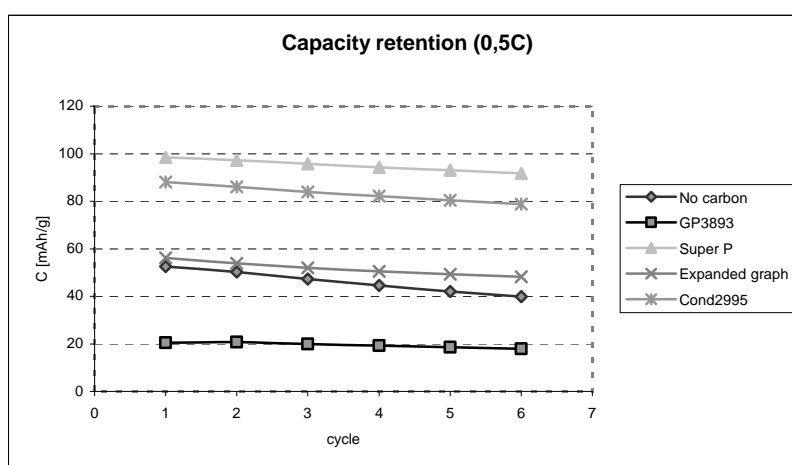


Fig.2 Discharge capacity in 5<sup>th</sup> cycle at discharge rate 0,5C

Fig.1 and Fig.2. are discharge voltage profiles of LiCoO<sub>2</sub> composite cathodes loaded with different conductive materials. The results indicate that with Super P best results was obtained and that polarization of Super P electrode is with comparison to the others highly reduced. Highest discharge capacity is acquired. It was proved that a higher discharge capacity and less polarization means lower internal resistance.

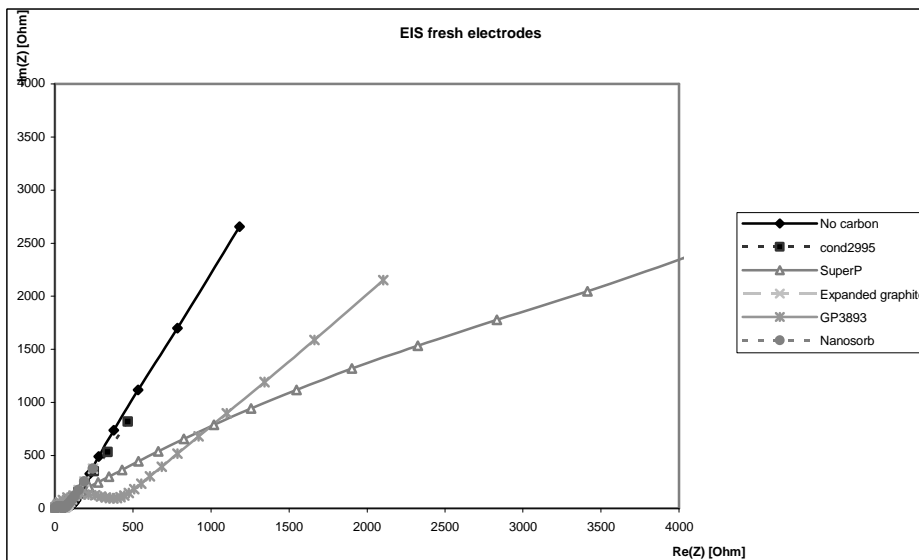
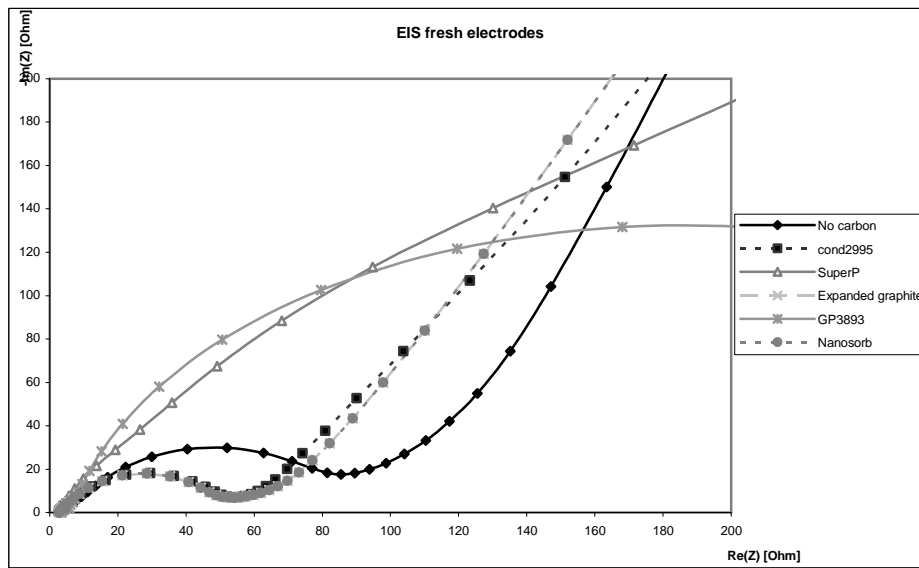
Cycle num.	No Carbon		GP 3893		Super P		Expanded graph		Cond2995	
	C [mAh/g]	Capacity retain [%]	C [mAh/g]	Capacity retain [%]	C [mAh/g]	Capacity retain [%]	C [mAh/g]	Capacity retain [%]	C [mAh/g]	Capacity retain [%]
1	52,5	100%	20,5	100%	98,5	100%	56,2	100%	88,1	100%
2	50,2	96%	20,7	101%	97,2	99%	53,8	96%	86,0	98%
3	47,3	90%	19,9	97%	95,8	97%	52,0	93%	84,0	95%
4	44,5	85%	19,3	94%	94,3	96%	50,5	90%	82,1	93%
5	42,0	80%	18,6	91%	93,0	94%	49,3	88%	80,4	91%
6	39,9	76%	17,9	87%	91,7	93%	48,2	86%	78,8	89%

Tab.1. Capacity retention at discharge rate 0,5C



### 3.2. IMPEDANCE SPECTROSCOPY

Ac impedance plots were made on fresh  $\text{LiCoO}_2$  composite electrode.



Impedance measurements were made on OCV potential half an hour after the cell was assembled. Usually, the impedance spectra are combination of distorted semicircle for high frequency response and straight line for low frequencies. The intercept with X axes at high frequencies is believed to be the total resistance related to the cathode material and electrolyte resistance. The straight part of spectrum is called Warburg impedance and it is associated with the lithium ion diffusion in the composite cathode.

It is astonishing, that material with best performance on cycling has among his EIS spectrum the worst diffusion parameters of all materials. It can be point out by higher transfer resistance of lithium ions due to mesoporous structure although mesopores can provide quick pathways for ions to penetrate. There will be discharge rate capabilities measurement performed to clarify mesoporous structure influence on EIS characteristics.

### 3.3. DISCUSSION

It was proved that carbon type influences electrochemical performance of composite electrodes in wide range thus choice of right carbon is crucial for best results. There are no evident performance differences between graphites (crystalline) and carbon blacks (amorphous). Undoubtedly one of the most significant factor is dispersion level of conductive additive in active material. Some specimens were even after long ball milling and ultrasonic mixing poorly dispersed and made sediments – Nanosorb, GP3893. Contrariwise, expanded graphite is composed by flake-like formations with low bulk density witch was hard to divide into small particles.

Best results were obtained by Super P (carbon black) and Cond 2995 (micromilled graphite). Super P was not overcame by any tested material both by capacity and retention.

### ACKNOWLEDGEMENT

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