

Behavior of Non-Graphitic Carbon Electrodes of Lithium-Ion Batteries in Electrolytes based on Ionic Liquids

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1. Introduction

Lithium-ion battery (LIB) has been one of the most promising electrochemical energy storage technologies [1, 2]. LIB works are based on the movement of lithium ions between two battery electrodes, the anode and cathode. The ions are stored in the anode which is often graphite. When they discharge, the ions move to the cathode. One advantage of a graphite anode is the small volume change that occurs when the ions enter it. Lithium-ion batteries (LIB) generally use electrolyte solutions based on organic solvents and LiPF_6 salt because they have high ionic conductivity, and can form an effective solid electrolyte interface (SEI) that helps intercalation of lithium ion into graphite anode. However, organic electrolytes involve safety issues because of their low thermal stability and flammability. Ionic liquids (ILs) are molten salts with melting points well below 100 °C. ILs have many useful properties, including low vapor pressure, high chemical and thermal stability, wide electrochemical voltage window, non-flammability and high ionic conductivity [3, 4]. However, incompatibility of typical ILs with graphite anode has also been recognized as a serious problem for lithium-ion battery application [5, 6]. Non-graphitic carbons such as hard carbon have an advantage that they can be intercalated/deintercalated in a different types of electrolyte [7, 8]. Besides, hard carbons show very small changes of volume during the charge/discharge. The anode based on hard carbon may be quite promising for the new generations of LIB with ILs. In this work, the behavior of non-graphitic carbons electrodes in solutions based on ILs was investigated.

2. Experimental

The hard carbon was prepared from table sugar by the method described in Ref. [9]. Sugar precursor (“sulfuric acid washed” sugar) was pyrolyzed from 600 – 1000 °C for 3 h in a high-purity argon atmosphere.

The active materials were mixed with the amount of 7-9 wt% polyvinylidene fluoride (PVDF) in N-methylpyrrolidone (NMP) solution. The resulting slurry was cast onto a copper foil, and a doctor blade with a gap opening of 200 μm was used to define the maximum thickness of the freshly coated layer. The resulting film was dried at 120°C in order to evaporate the NMP. The electrodes were compacted to the desired density by calendaring. The thicknesses of the active layers of electrodes were in the range 0.08- 0.10 mm. The disc electrodes having a diameter of 16 mm were cut out of the coating film cast onto metal foil current collector using a punch. Before assembling the cell the electrodes were dried under a primary vacuum at 120°C in the time frame of 12 h. The coin cells (CR2016 standard size) were assembled in an argon-filled glove box (Unilab model, MBraun, USA). The TEKLON™ EDEX separator (manufactured by ENTEK Membranes LLC, USA). The electrolyte 1M LiPF₆ in EC:DEC:DMC=1:1:1 w/w electrolyte (conventional electrolyte), as well as the electrolytes based on the following ILs from ENEA (Rome/Casaccia, Italy): N-methyl-N-propyl pyrrolidinium bis(fluorosulfonyl)imide (PYR13FSI) and N-methyl-N-butylpyrrolidinium bis(trifluoromethanesulfonyl)imide (PYR14TFSI) were used for assembling the coin cells. Electrochemical investigations were performed using a 32-channel battery cycler MSTAT 32 from Arbin Instruments, USA and multi-channel potentiostat VMP3 from Princeton Applied Research, UK.

3. Result and discussion

Herein, we report a hard carbon synthesized via carbonization of table sugar. The apparatus for carbonization is a simple horizontal furnace with a homogeneous heating zone of 150mm and a quartz tube (20mm diameter) presented schematically in the Figure 1. A thin layer of the precursor powder is spread uniformly on ceramic plate which is introduced in the quartz tube reactor. For example hard carbon is

obtained from the pyrolysis of sugar at different temperatures ranging from 600 to 1000°C. The selected temperature was reached with a heating ramp of 10°C/min and using an argon flow. Finally, the system is cooled down at 5°C/min under argon flow. In some cases, additional thermal treatments were also performed on the purified carbon materials.

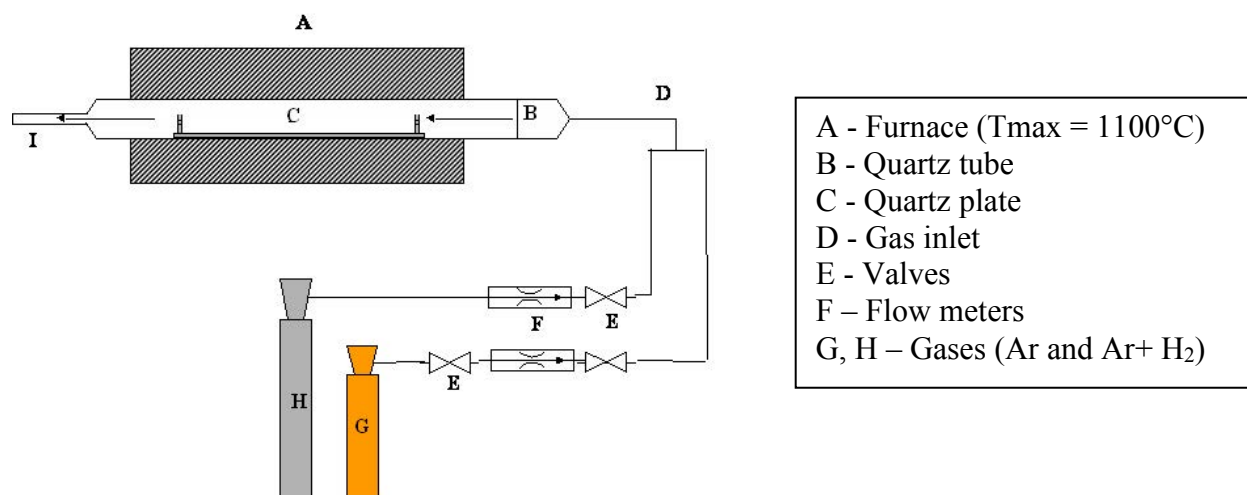


Fig. 1. Schematic representation of the unit used for synthesis of anodic materials

A scanning electron microscope (SEM) was used to examine the powder morphology of hard carbon obtained from the pyrolysis of table sugar. The SEM is represented by Fig 2. Hard carbon has small particles which come in particle sizes lower 20 μm.

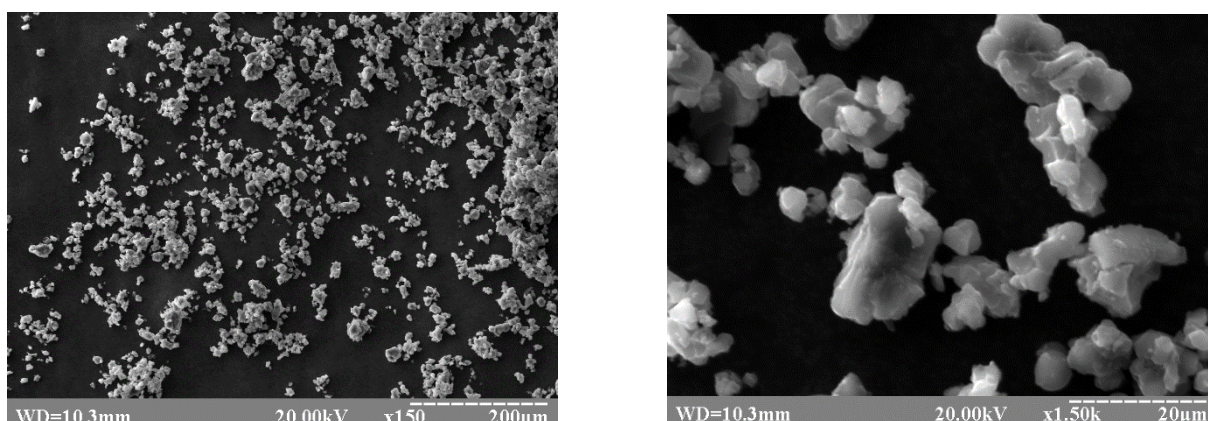


Fig. 2. SEM of hard carbon obtained from the pyrolysis of table sugar at 1000 °C

The electrochemical performance of hard carbon anode has been evaluated using

different electrolyte mixtures. Figure 3 (red line) shows potential vs. capacity for lithium insertion/extraction from conventional electrolyte and Fig. 3 (blue line) shows the corresponding results for lithium insertion/extraction in IL based electrolyte (PYR13FSI). The reversible part of the potential profiles for both cell and lithium insertion and extraction has a similar shape with some differences in potential values. The focus of this work was reversible capacities, it should be note that the irreversible capacities of cell using IL based electrolyte was higher than that for the cell with conventional electrolyte.

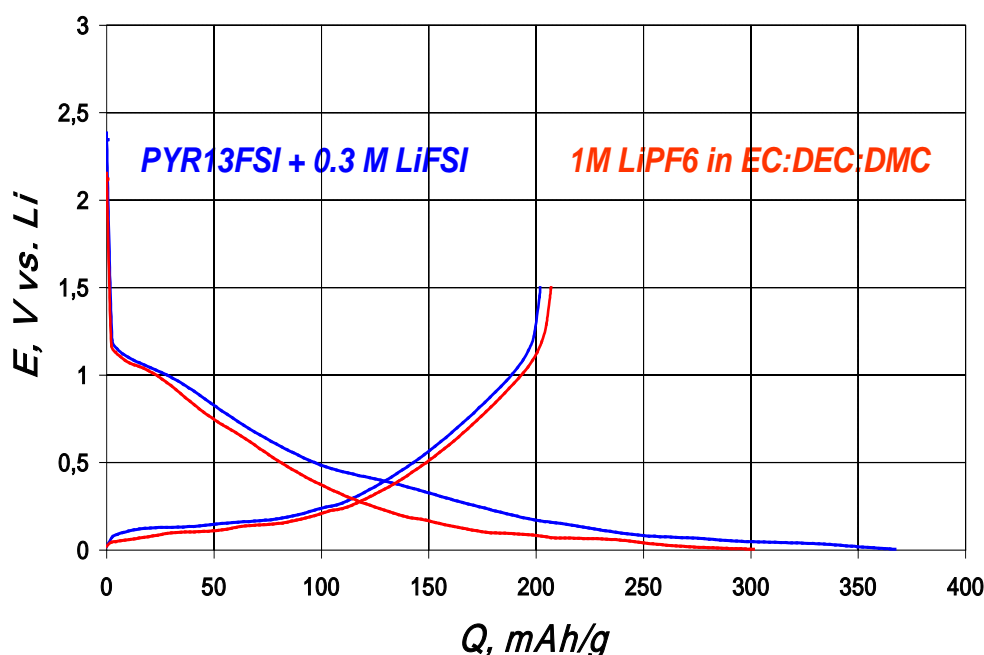


Fig. 3. Profiles of charge/discharge potentials of the hard carbon at current density 30 mA/g into organic (red line) and IL based electrolyte (blue line)

Thus, the lithium insertion/ removal process is not completely reversible in the case IL based electrolyte. The initial capacity of hard carbon in lithium deintercalation was found to be of 208 A·h·g⁻¹ within the range of cut-off potentials from 0.0 to 2.0V. The irreversible capacity was about 94 mA·h·g⁻¹, which is less than in the case of IL based electrolyte. Table 1 shows electrochemical characteristics for the sugar samples pyrolyzed at different temperature. The difference in capacity between the first discharge and the first charge (Q rev.) gives the irreversible capacity (Q irr.). Table 1 shows that the samples have different irreversible Li

insertion capacities. The carbonization temperature significantly influenced on the irreversible capacity for lithium storage. The difference of reversible capacity is small for all samples. The irreversible capacity is small for samples obtained at higher temperature. The irreversible capacity is not only a measure of the amount of SEI, but can also relate to the reduction of surface species on the carbon [10]. Thus, there are no interests to use lower temperature treated samples for further investigation.

Table 1. The electrochemical properties of hard carbon obtained at different temperature

#	T, °C	Electrolyte	Q _{rev} , mA·h·g ⁻¹	Q _{irr} , mA·h·g ⁻¹	Efficiency on 1st cycle, %	Efficiency on 10 st cycle, %
1	600	LP71	195	341	36	89
2	700	LP71	191	223	46	93
3	800	LP71	203	156	57	96
4	900	LP71	206	115	64	98
5	1000	LP71	208	94	69	98
6	1000	PYR13FSI	202	167	55	91
7	1000	PYR14TFSI	32	98	-	-
8	1000	PYR13FSI+5% LP71	199	106	65	96
9	1000	PYR14TFSI+5%LP71	174	120	59	93

LP71:1M LiPF₆ in EC:DEC:DMC=1:1:1 w/w

PYR13FSI: 0.3 M LITFSI in N-methyl-N-propyl pyrrolidinium bis(fluorosulfonyl)imide

PYR14TFSI: 0.3 M LITFSI in N-methyl-N-butylpyrrolidinium bis(trifluoromethansulfonyl)imide

In order to investigate the electrochemical behavior of hard carbon, in our studies mixture conventional electrolyte and IL-based electrolytes have been tested. Our findings are presented in the table 1 for the sugar sample pyrolyzed to 1000°C. It can be seen from the table that organic electrolyte content in the IL based electrolyte causes increasing the capacity and decreasing the irreversible capacity. Thus the organic additives may improve electrochemical performance materials in IL based electrolyte.

For all electrochemical test results described in this section, we used one grade of graphitized carbon materials. This is PUREBLACK® 205 Carbon received from

Superior graphite Co (USA). A transmission electron microscope (TEM) and a scanning electron microscope (SEM) were used to examine the powder morphology of PUREBLACK® 205 Carbon. The SEM and TEM are represented by Fig 4. Similar to Carbon Black Pureblack has spherical particles which come in particle sizes lower 20 μm (see Fig. 4 left picture). We would like to note very unusual appearance of the graphitic structures shown in TEM (Fig. 4 right picture). Noting their graphite-like composition (at a given particle size of below 100 nm), one should expect to see them as being more conductive than hard carbon.

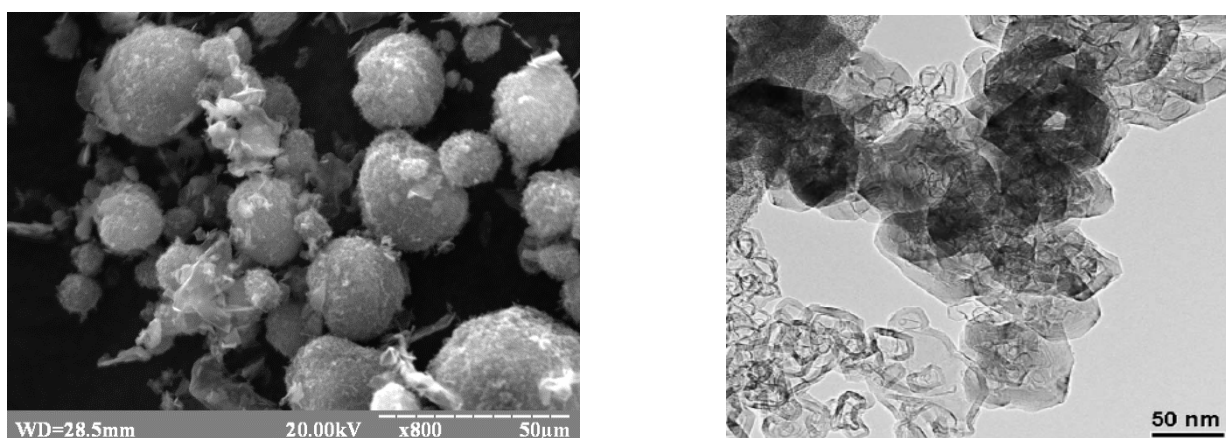


Fig. 4. SEM (left picture) and TEM (right picture) of PUREBLACK® 205 Carbon.

Thus the graphitized carbon black (Pureblack), being an ultra pure partially graphitized carbon black with properties exceeding those of battery grade acetylene blacks have higher conductivity than carbon black and feature higher packing density. The PUREBLACK Carbon is quite an interesting material for development of LIB.

Figure 5 shows the voltage profiles of PUREBLACK® 205 Carbon at the current density of 30 mA/g. The experiment was conducted in the CR2016 coin cells with a Li metal counter electrode. The initial capacity of PUREBLACK in deintercalation of lithium was seen to be 192 mA·h/g within the range of cut-off potentials between 0.0 and 2.0 V. The capacity that cannot be recovered (the "irreversible capacity loss") is observed in the first charge/discharge cycle. It is clear from Fig. 5 that the irreversible capacity in the first cycle is very high (up to 215 mA·h/g). The irreversible capacity exists mainly due to the growth of solid-electrolyte interface (SEI) film. Such types

of materials are characterized by presence of a large potential plateau at the potentials of about 0.8 V in their intercalation profiles in the first cycle (Fig. 5). The formation of SEI film is related to a surface area. As for the PUREBLACK, it has a large specific surface area (of about $50 \text{ m}^2 \cdot \text{g}^{-1}$). Therefore, the formation of SEI film would certainly lead to a high irreversible capacity in the PUREBLACK.

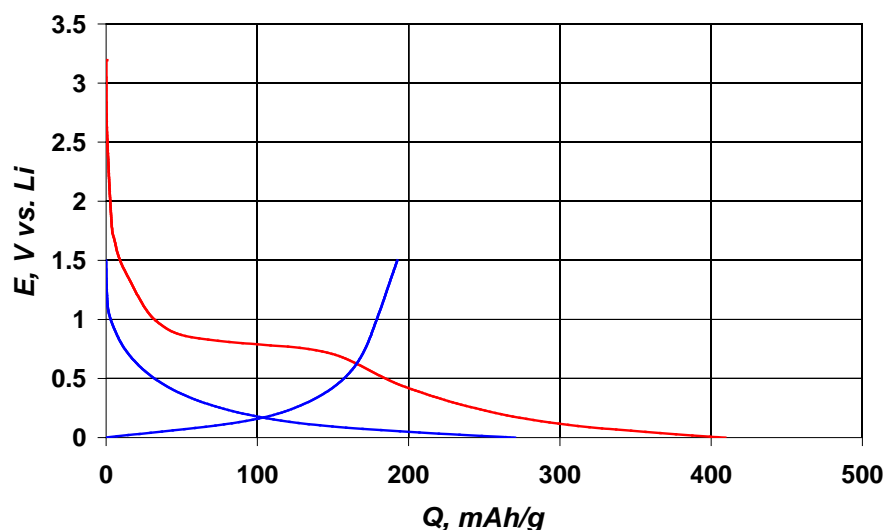


Fig. 5. The profiles of charge/discharge potentials for PUREBLACK[®]205 Carbon at the current density of 30 mA/g. Electrolyte: LP71

The data presented in table 2 shows that the difference in capacity between the first discharge and the first charge was higher than for cell with conventional electrolyte. The organic additive of organic electrolyte (LP-71) improved electrochemical performance of PUREBLACK in IL based electrolyte but that effect was lower than for hard carbon materials (see table 1).

Table 2. The electrochemical performance of PUREBLACK[®] 205 Carbon in the IL based electrolytes

Electrolyte	Q _{rev} , mA·h·g ⁻¹	Q _{irr} , mA·h·g ⁻¹	Efficiency on 1st cycle, %	Efficiency on 10 st cycle, %
PYR13FSI	98	245	29	88
PYR14TFSI	22	116	16	76
PYR13FSI+5%LP71	115	267	30	93
PYR14TFSI+5%LP71	103	272	27	89

4. Conclusion

The non-graphitic carbon materials were prepared. Their electrochemical properties in the commercial electrolyte and IL were studied by the constant current charge-discharge test. The carbon anode exhibited lower reversible capacity in IL electrolytes than that in conventional electrolyte. In order to overcome this problem and to improve electrochemical property anodes, in the current work mixed electrolytes containing non-flammable IL were prepared and investigated. The organic additive of organic electrolyte (LP-71) improved electrochemical performance of non-graphitic carbon materials in IL based electrolyte but still characteristics of materials were lower than in conventional electrolyte. Thus, further optimization materials and composition of IL based electrolyte are required.

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