



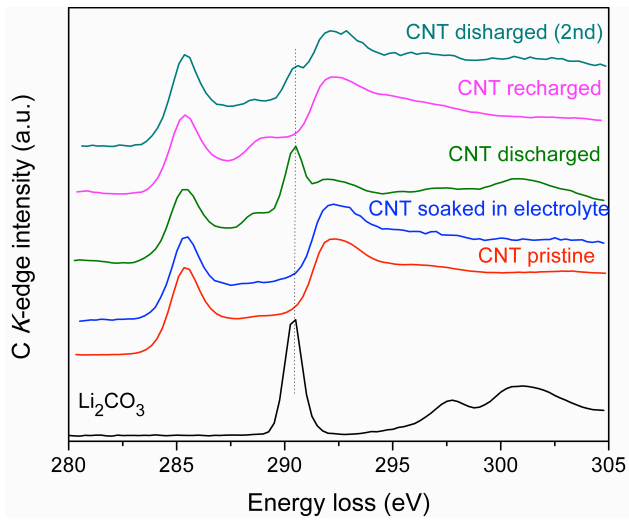
	<b>Experiment title:</b> X-ray Raman Scattering Measurements of Different Li-ion Battery Electrolyte Solutions	<b>Experiment number:</b> CH-4573
<b>Beamline:</b> ID20	<b>Date of experiment:</b> from: 18.11.2015 to: 24.11.2015	<b>Date of report:</b> 24.02.2016
<b>Shifts:</b> 18	<b>Local contact(s):</b> Blanka Detlefs	<i>Received at ESRF:</i>
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## Report:

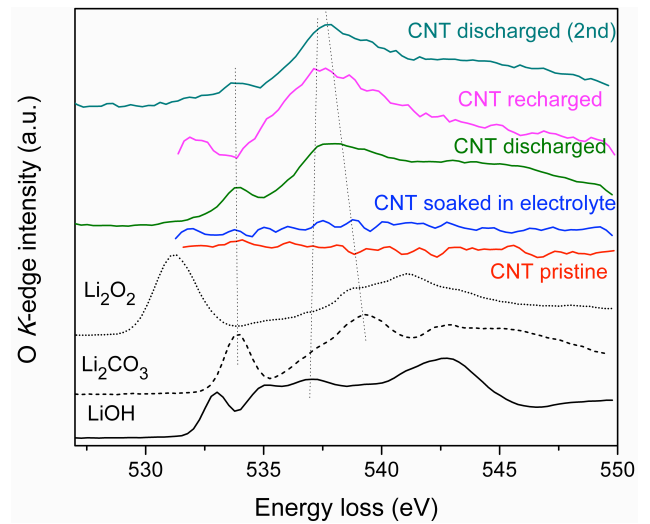
Electrolyte solutions of lithium salts in mixed organic solvents are of great importance for the development of Lithium-ion batteries (LIBs). Battery performance is strongly influenced by the characteristics of the electrolyte and its components [1-3]. In this work, we have probed how the electronic structure of electrolyte solution is affected by different salt concentrations. Different mixtures of LIB electrolyte solutions were investigated via X-ray Raman Scattering (XRS) technique combined with liquid jet for the first time. Besides, the electronic structure of some cathode materials for Li-O<sub>2</sub> batteries was probed by *ex-situ* XRS measurements to identify the side products.

The elastic energy was set to 9.69 keV with Si (660) analyzers. XRS data with the energy resolution of ~ 700 meV were collected by scanning the incident beam energy. The beamsize on the sample was ~ 8 (V) μm×16 (H) μm and the intensity was 4×10<sup>13</sup> photons/s.

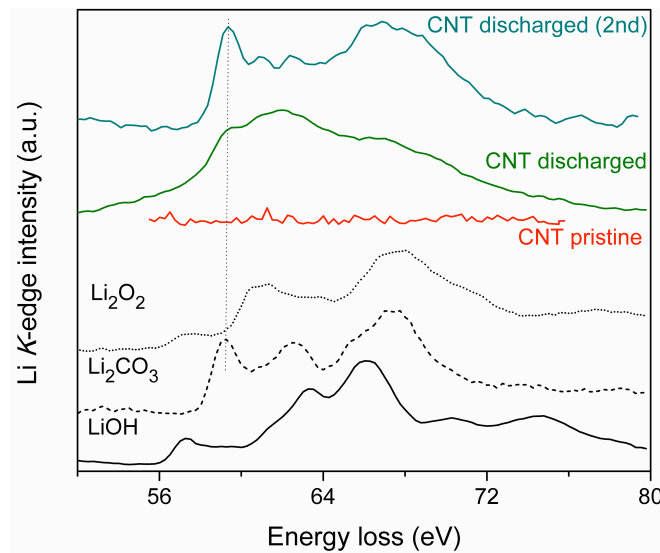
The electrolyte solutions were different molarities of LiPF<sub>6</sub> salt (1M and 2M) in EC (Ethylene Carbonate):DMC (Dimethyl Carbonate) (1:1 vol.), 1M LiPF<sub>6</sub> in PC (Propylene Carbonate), pure solvent EC:DMC (1:1 vol.) and PC. The liquid samples were filled into the flow cell which had a capillary with the diameter of 1.5 mm. A closed circle flow cell designed at ESRF [4] was used for the liquid sample measurements. For the cathode materials, carbon nanotubes (CNTs) at different conditions (pristine, soaked in electrolyte, discharged, recharged, and discharged 2<sup>nd</sup> time) were investigated. Thin pellets of CNTs were placed in a small chamber which was coated with Kapton foil windows. Li<sub>2</sub>CO<sub>3</sub>, Li<sub>2</sub>O<sub>2</sub> and LiOH were used as reference materials. The reference powder materials were measured in quartz capillaries with the diameter of 0.5 mm and 1.0 mm. All the sample preparation process was carried out in a glove box filled with dry argon atmosphere.



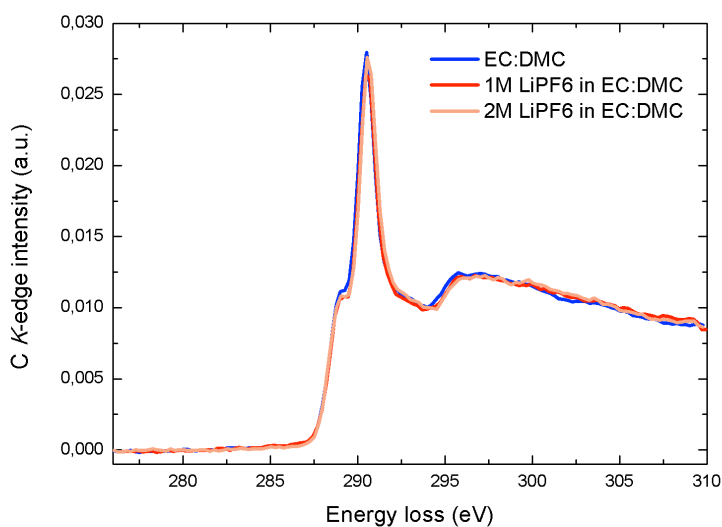
**Fig.1.** The C *K*-edge XRS spectra of the CNTs and  $\text{Li}_2\text{CO}_3$



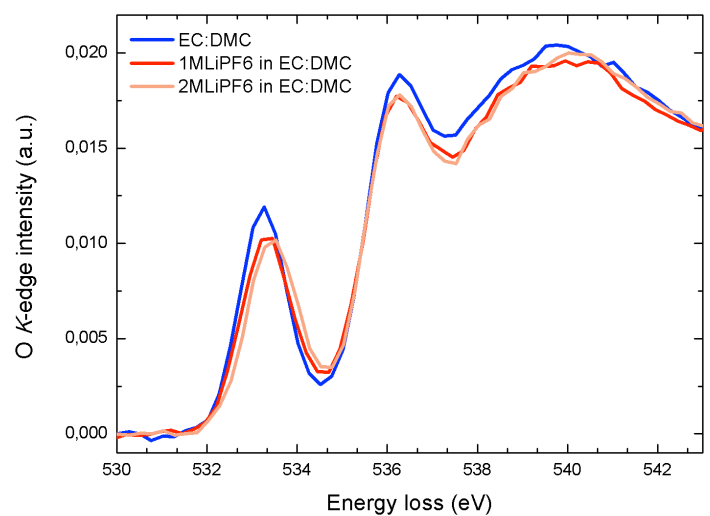
**Fig.2.** The O *K*-edge XRS spectra of the CNTs,  $\text{Li}_2\text{CO}_3$ ,  $\text{Li}_2\text{O}_2$  and LiOH



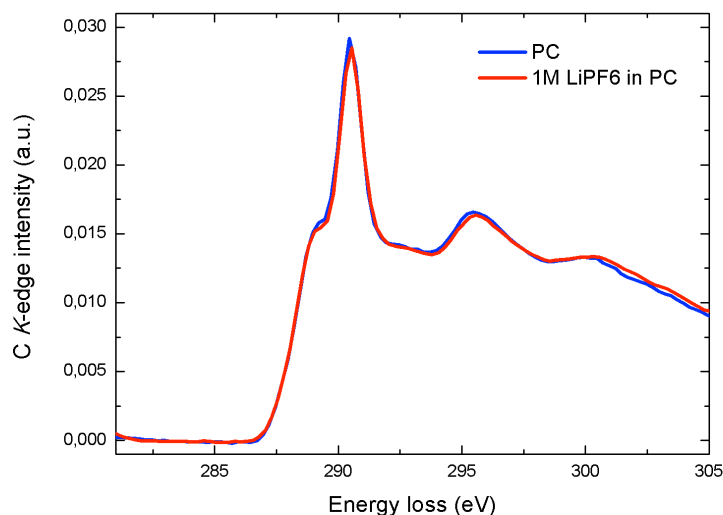
**Fig.3.** The Li *K*-edge XRS spectra of CNTs,  $\text{Li}_2\text{CO}_3$ ,  $\text{Li}_2\text{O}$  and LiOH



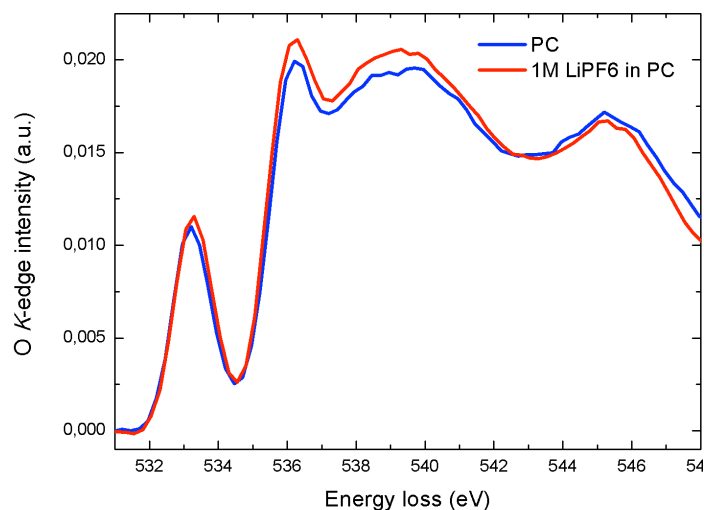
**Fig.4.** The C *K*-edge XRS spectra of pure EC:DMC (vol. 1:1) and different molarities of  $\text{LiPF}_6$  (1M and 2M) in EC:DMC (vol. 1:1)



**Fig.5.** The O *K*-edge XRS spectra of pure EC:DMC (vol. 1:1) and different molarities of  $\text{LiPF}_6$  (1M and 2M) in EC:DMC (vol. 1:1)



**Fig.6.** The C *K*-edge XRS spectra of pure PC and 1M LiPF<sub>6</sub> in PC



**Fig.7.** The O *K*-edge XRS spectra of pure PC and 1M LiPF<sub>6</sub> in PC

The CNTs were investigated by *ex-situ* XRS measurements to identify the product Li<sub>2</sub>O<sub>2</sub> and the side products LiOH and Li<sub>2</sub>CO<sub>3</sub> formation after charge and discharge of the CNT electrodes. Fig.1-3 show the comparison of reference materials with CNTs at different conditions for C *K*-, O *K*- and Li *K*-edges. According to the XRS results, Li<sub>2</sub>CO<sub>3</sub> is the dominant side product after discharge. In addition to Li<sub>2</sub>CO<sub>3</sub>, Li<sub>2</sub>O<sub>2</sub> is also observed as the discharge product in CNT cathodes taken from the Li-O<sub>2</sub> battery test cells after 1<sup>st</sup> discharge. Recently, similar experiments on CNTs have been performed by Yilmaz *et al.* using x-ray absorption spectroscopy (XAS) [5]. The results of XAS and XRS measurements are comparable and in an agreement. Here, we showed XRS measurements are suitable for this system and for the future *in-operando* experiments can be performed in designed electrochemical cells for Li-O<sub>2</sub> batteries.

C *K*- and O *K*-edges XRS spectra of each different electrolyte solution are presented in Fig. 4-7. C *K*-edges XRS spectra of pure PC and EC:DMC do not exhibit any significant shift with addition of the lithium salt (Fig.4 and Fig.6). In the O *K*-edge XRS spectra of pure solvents and their solutions with LiPF<sub>6</sub> (Fig.5 and Fig.7), the first and second sharp peaks near 533 eV and 536 eV represent transitions from the carbonyl and ring oxygen atoms to the  $\pi$ -antibonding system ( $\pi^*$ ), respectively. Transitions from both carbonyl and ring oxygen atoms ( $1s-\sigma^*$ ) contribute to the broader third and fourth peaks in the same spectra. Among these features, only the carbonyl  $1s-\pi^*$  transition near 533 eV exhibits energy shift upon addition of lithium salt. Increasing the Li salt concentration does not affect the transitions from the ring oxygen atoms. In Fig.5, the carbonyl  $\pi^*$  peak (533.28 eV) shifts 0.07 eV for 1M Li salt and 0.17 eV for 2M Li salt, relative to pure EC:DMC. In Fig.7, the shift is 0.1 eV with the addition of Li salt for the carbonyl  $\pi^*$  peak (533.2 eV). The influence of Li<sup>+</sup> cations on the solvent electronic structure is seen as a shift for the carbonyl  $\pi^*$  feature toward higher energy loss values in the O *K*-edge spectra [6].

Li *K*-, C *K*- and O *K*-edges XRS spectra of different electrolyte solutions and cathode materials provide a fingerprint-like spectra for the next measurements. This study will contribute to a better understanding of electronic structure of LIB electrolyte, before the individual components of the electrolyte solution decomposes under applied voltage. After probing the nature of individual components of LIBs, the main purpose will be to characterize the dynamics of LIB through *in-situ* XRS experiments.

**References:** [1] D. Aurbach *et al.*, *Electrochimica Acta* 50, 247-254 (2004). [2] S.S. Zhang *et al.*, *Journal of Power Sources* 107, 18-23 (2002). [3] D. Aurbach *et al.*, *Journal of Power Sources* 165, 491-499 (2007). [4] Ch. J. Sahle *et al.*, *J. Synchrotron Rad.* 22, 1-4 (2015). [5] E. Yilmaz *et al.*, *Nano Lett.*13, 4679-4684 (2013). [6] J. W. Smith *et al.*, *Phys. Chem. Chem. Phys.* 16, 23568-23575 (2014).