In-situ Raman spectroscopic study of pyrolysed phenolic resin for lithium-ion batteries

D. Goers[a)], L. Hardwick[a, b)], M. C. Baertsch[a)], and
P. Novák[a)]

[a)] Paul Scherrer Institute, Laboratory for Electrochemistry, CH-5232 Villigen PSI, Switzerland
[b)] Department of Chemistry, University of Southampton, Highfield, Southampton, Hampshire, SO17 1BJ, England

Carbons, particularly MCMB's and graphites, are still the first choice for negative electrode materials in lithium-ion batteries because of their high specific charge, good cycleability and low cost. In recent years, carbons made by heat-treatment of various natural sources (coffee beans, coconut shells) and polymeric materials (polyfurfuryl alcohol, phenolic resin) have received more interest. These materials allow insertion of lithium into small cavities in their structure and often offer specific charges even higher than the theoretical value of graphite (372 Ah/kg) [1]. In this work we present the electrochemical behaviour of carbons made by pyrolysis of duroplastics and their characterisation using Raman spectroscopy.

Phenolic resin was subjected to curing at 0.3 K/h from 20 to 100 °C, reduced to small pieces (approximately 1 mm diameter) and heat-treated to 800 °C with a temperature rate of 5 K/min. The material was maintained at 800 °C for 2 h, and then ground to a fine powder (10 µm diameter) by milling.

In-situ Raman spectroscopy was performed in order to study the lithium insertion process into this carbon. A specially designed cell consisting of a lithium counter- and reference electrode, a polypropylene separator and a carbon electrode was used to collect Raman spectra. The electrolyte solution was 1M $LiClO_4$ in ethylene carbonate (EC) : dimethyl carbonate (DMC) 1:1 (w:w).

Figure 1 presents the electrochemical behaviour of the first lithium insertion into pyrolysed phenolic resin under galvanostatic conditions. In contrast to graphite no staging phenomena could be observed [2].

Figure 2 shows in-situ Raman spectra in the frequency range of 1000 – 1800 cm^{-1}, taken from one arbitrarily selected point on the sample. The spectra were recorded during the galvanostatic examination shown in figure 1.
The deconvolution of the open circuit spectra reveals the presence of four bands at 1224 cm^{-1}, 1370 cm^{-1}, 1570 cm^{-1} and 1645 cm^{-1}. The band around 1370 cm^{-1} indicates a high presence of amorphous carbon structures. Graphitised structures can be observed at ca. 1570 cm^{-1}. The band appearing at 1645 cm^{-1} could arise from oxidation-induced disorder of carbon [3]. This band shifts to lower wavenumbers indicating changes in the surface structure during the lithium insertion.

From the changes observed in the in-situ Raman spectra it can be concluded that during lithium insertion structural modifications occur in the pyrolysed phenolic resin.

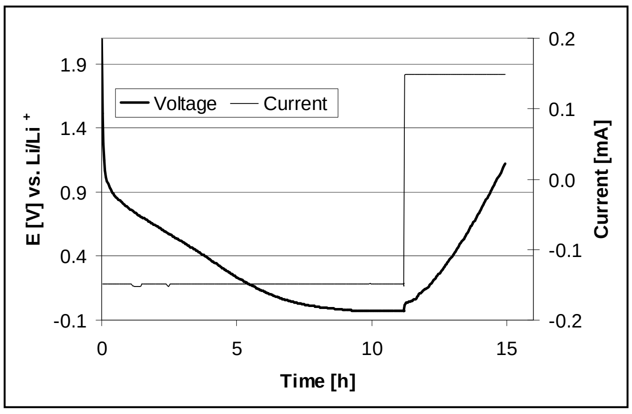

Figure 1: First galvanostatic lithium insertion into a phenolic resin-based carbon material (charge rate C/5, between 1.5 V and -30 mV vs. Li/Li^+). The lithium insertion step was stopped during lithium plating.

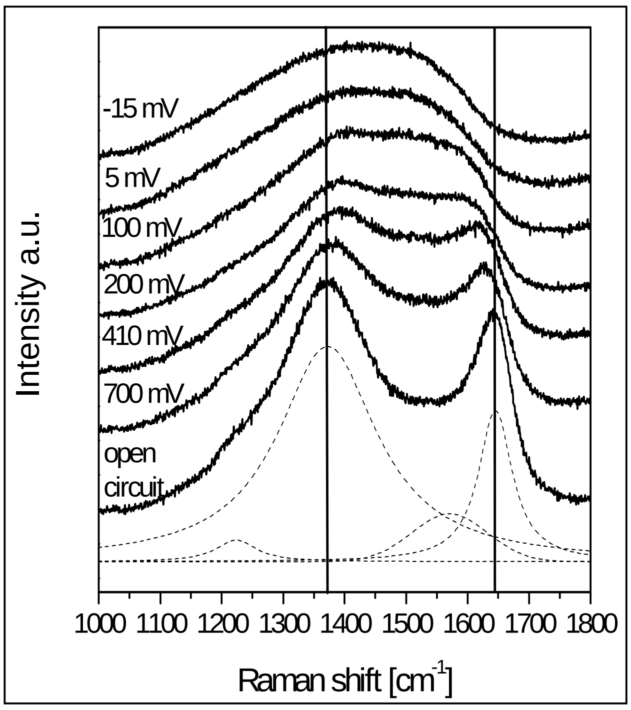

Figure 2: In-situ Raman spectra of phenolic resin-based carbon during the first galvanostatic lithium insertion (C/5 rate). The spectra were taken using a LabRAM confocal Raman spectrometer (Jobin Yvon) equipped with a HeNe laser at 632.8 nm and arbitrarily shifted along the y-axis. The spectra were measured at the same point throughout the cycling (time/spectra: 60 s, 3-8 Accumulations, laser power 900 µW). Curve analysis was carried out using Microcal Origin Peak Fitting Module (Fitted bands are included as dashed lines for the open-circuit spectra). The assigned potentials were measured vs. Li/Li^+.

---

[1] G.T.K. Fey, Y.C. Kao, *Mat. Chem. and Physics* 73 (**2002**) 37

[2] M.Winter, J.O. Besenhard, M.E. Spahr, P. Novák, *Adv. Mat.* 10 (**1998**) 725

[3] F. Kong, R. Kostecki, G. Nadeau, X. Song, K. Zaghib, K. Kinoshita, F. McLarnon, *J. Power Sources* 97-98 (**2001**) 58