Investigation of $LiMn_2O_4$ Cathodes in Liquid and in Gel Electrolyte by Electrochemical Impedance Spectroscopy

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In recent years, electrochemical impedance spectroscopy has been used extensively to electrochemically characterise intercalation compounds such as $LiMn_2O_4$, mostly in liquid electrolyte and at room temperature, even though commercial batteries today include gelbased electrolytes and are operating under a wide range of temperatures. The impedance response has been described by various, sometimes conflicting, models, most often by equivalent circuit elements [1], but also by mathematical models based on fundamental properties [2]. For example, in order to validate the suggested models in the literature, the impedance response has been measured in front- and on the back-side of the electrode, simultaneously [3]. This work and other measurements[4]conducted in our group showed that none of the existing suggested models fully could explain the experimental behaviour. Therefore, we believe that there is still a need for further investigations to clarify the reaction mechanism and the rate limiting processes of $LiMn_2O_4$.

In this work, the impedance response of $LiMn_2O_4$ in gel electrolyte is examined over a wide range of temperatures. The results are compared with results obtained in liquid electrolyte.

Experimental

EIS-measurements at open-circuit potential were carried out using a three electrode cell with $LiMn_2O_4$ (80 wt% $LiMn_2O_4$, 15 wt% carbon black and 5 % EPDM) as working electrode, lithium foil as counter- and reference electrode, respectively. The electrolytes used are 1 M $LiBF_4$/1:1 EC:DEC and a mixture of 24 wt% PMMA (M_n=38.000) in 1 M $LiBF_4$/1:1 EC:DEC. The frequency was varied between 60 kHz to 6 mHz and the AC-amplitude was set to 5 mV. The experiments were performed at different depth-of-discharge (DOD) and at various temperatures (-5<T<60 °C).

Results

Figure 1 and 2 show examples of Nyquist plots measured at different temperatures (T=-0.2, 3, 10, 24 and 56 ºC) at DOD=0.75 with a precycled composite electrode of $LiMn_2O_4$ in gel electrolyte. It can be established that the temperature has a great influence on the number of time-constants that can be clearly distinguished in the spectra. Also, it can be seen that the impedance behaviour in gel is different from what is normally observed in liquid electrolyte [1]. Furthermore, to increase the understanding of the impedance spectra, further impedance measurements have been run using different configurations of the electrode and the results will be compared and discussed.

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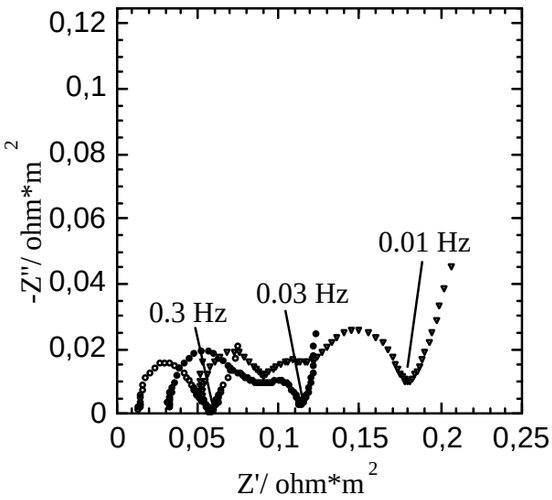

Figure 1. Nyquist plots obtained with a composite electrode of $LiMn_2O_4$ in gel electrolyte at DOD=0.75 and at ○ 56 ºC● 24 ºC ∇10 ºC

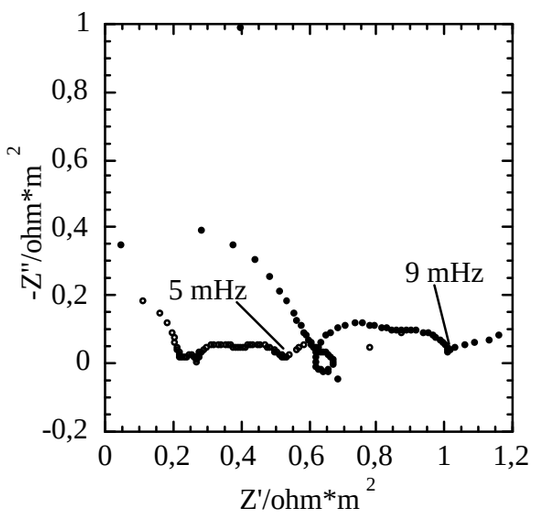

Figure 2. Nyquist plot obtained with a composite electrode of $LiMn_2O_4$ in gel electrolyte at DOD=0.75 and at ○ 3 ºC ● -2 ºC