ELECTROCHEMICAL 1 M PEDANCE SPECTROSCOPY ANJ) INVESTIGATION OF 1 NTERFACIAL, PROCESSES IN LITI 11 UMRECHARGEABLE CELLS

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It is well known that the performance and cycle life of lithium rechargeable cells arc governed by interfacial processes such as charge-transfer, passive film formation, ionic diffusion, chemical modification of electi olyte components, and specific adsorption. Understanding of these processes have been important in deter mining the mechanisms of failure and have provided directions for improvement of performance and cycle life.

Of the numerous instrumental methods available to the electrochemist only a few arc readily applicable for the investigation of processes in two-terminal batteries. Among the steady-stat c methods, electrochemical impedance spectroscopy (1 3I S) has been widely applied. in an EIS exper iment the two terminal cell impedance, Z, and phase angle differ ence (between the applied sinusoidal voltage and observed sinusoidal ccl] cur rent) ,φ, arc measured as a function of a frequency of the applied sinusoidal voltage, ω. The plot of $Z\cos\varphi$ (also called Z' or Z_{real}) vs. $Z\sin\varphi$ (also called Z'' or $Z_{imaginary}$) at various fi equencies is commonl y present ed as impedance data. Analysis of such impedance results is either based on mathematical modelling of the processes or by regression of obser ved responses to elect rical equivalent circuit models. 'I 'he lat ter approach is appears to be very common. In principle, both appr oaches yield identical values as they start with the same phenomenological models for the system, In determining the parameters for the various processes, the expel-imcntal data must be statistically significant and the presence of non- stationar y processes must be recognized. The modification of experimental data by the foregoing factors is particularly significant in the area of lithium batteries where pr ocesses such as film formation, electrolyte decomposition, slow diffusion and self-discharge make the results time-dependent. The application of statistically formulated measurement models[1] to the regression analysis can improve the reliability of the information obtained from the impe.dance spectra and also detect non-stationary processes. in this paper wc critically review the results of EIS for the investigation of the various int erfacial processes in lithium rechargeable cells.

The basic processes occurr ing at the anode/electrolyte interface during nor mal cell operation arc : 1. charge transfer (ionization of lithium, deposition of lithium metal, electrochemical insertion into host matrix such as carbon); **2.** formation of passive films by electrochemical reaction of lithium with the electrolyte; 3. ionic conduction and diffusion of lithium and other ions through solid electrolyte layers on the electrode. Charge transfer must obviously occur where both the oxidized and reduced species arc available. The lithium ions arc found in the solid electrolyte layer adjacent to the electrode