

Electrochemical Impedance Spectroscopy #5 Investigation of the Mechanism of Electrointercalation of Lithium Ions in TiS_2 Electrodes

Purpose

Electrodes that are capable of intercalating lithium ions are of interest as electrodes for secondary (rechargeable) lithium batteries, both anodes (e.g., graphite and other forms of carbon) and cathodes (e.g., TiS_2 , CoO_2 , NiO_2 , Mn_2O_4 , and V_6O_{13}). In such electrodes, the lithium ions are incorporated into the electrode material; this is accompanied by the addition of electrons in order to compensate for the change in charge. Although there have been many publications on the change in the structure of the electrode upon intercalation and on the diffusion of the intercalating ions within the electrode, there has been little work done on the mechanism of the electrointercalation reactions; that is, the processes that occur at the interface of the electrode and the electrolyte. These processes are discussed in this Capsule.

Reference

The Mechanism of Electrointercalation, P.G. Bruce and M.Y. Saidi, *J. Electroanal. Chem.* 332 (1992) 93-105.

Method

EIS is a powerful method for investigating processes occurring at the electrode/electrolyte interface. Since a range of frequencies is used, processes occurring at different rates (e.g., diffusion across the electrode surface and charge transfer at the electrode surface) can be detected within one experiment.

Results

Two intercalating electrodes, TiS_2 -L and TiS_2 -C, were used in this study (both are polymorphs of titanium disulfide). The impedance spectrum of the former is shown as a function of time in F1. At both time points, the spectrum consists of two overlapping semi-circles with a straight line at the low frequency limit.

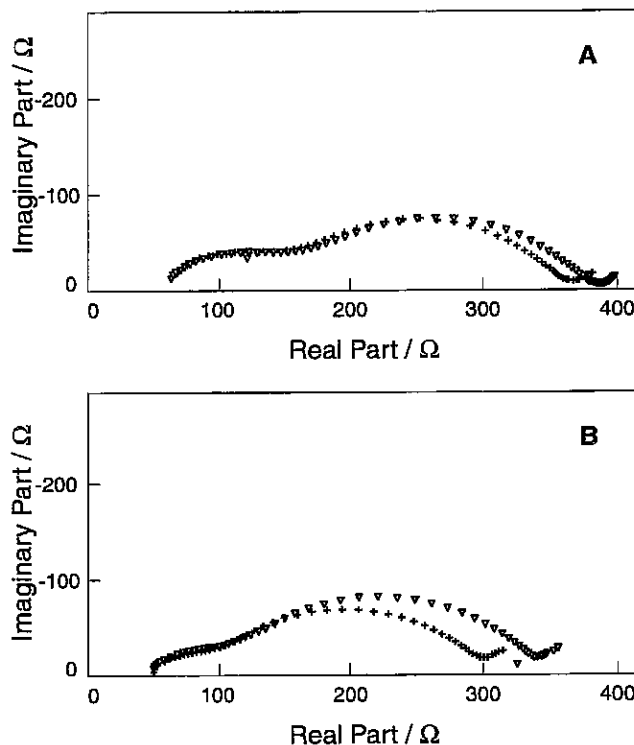


Figure 1. Impedance spectra for $\text{Li}_{0.15}\text{TiS}_2\text{-C}$ (A) and $\text{Li}_{0.12}\text{TiS}_2\text{-L}$ (B) in 1.4 M $\text{LiAsF}_6/2\text{-methyl THF}$ at time 0 (+) and after 48 hours (∇).

Two models were used as a basis for interpreting these spectra: the surface layer model and the ad-atom model. The first model is based on the observation that ionically conducting layers often grow on the surface of intercalating electrodes as a result of electrolysis of the electrolyte; hence a lithium ion must diffuse through this film and undergo a charge transfer reaction on the electrode surface. These processes can be modeled using an equivalent circuit shown in F2. In addition to the standard Randles circuit components (the electrolyte resistance (R_u), the double layer capacitance (C_d), the charge transfer resistance (R_{ct}), and an element due to mass transport (Z_w) (in this case, Z_w represents diffusion

of the lithium ions through the electrode)), there is a parallel RC combination (R_{sl} and C_{sl}) associated with the surface film. Although this equivalent circuit does provide a good match with the experimental data (provided C_{dl} is replaced by a constant phase element), the values for the circuit components are too large to be acceptable. This model was therefore considered to be incorrect.

The adatom model is based on the following processes: a solvated ion in the interfacial region loses part of its solvation shell and becomes adsorbed to the electrode surface. This latter process is accompanied by an electron transfer reaction into the host lattice in order to preserve electroneutrality (it has been shown by NMR that lithium exists in its ionic form in such intercalation lattices (1)). This adsorbed ion (adion) diffuses across the electrode surface to a suitable site, at which point it loses its remaining solvent molecules and becomes incorporated into the lattice.

The above processes were modeled using the equivalent circuit shown in F3. In addition to the standard Randles circuit components, there is R_{latt} , which represents the incorporation of the adatom/adion into the lattice; C_s , a pseudo-capacitance associated with the adatoms/adions; and Z_s , which represents the diffusion across the electrode surface. This model also provided a good fit with the experiment data, again provided that a constant phase element was included. In contrast to the surface layer model, the values for the circuit components were consistent with previously reported values, and hence this circuit was considered to be correct.

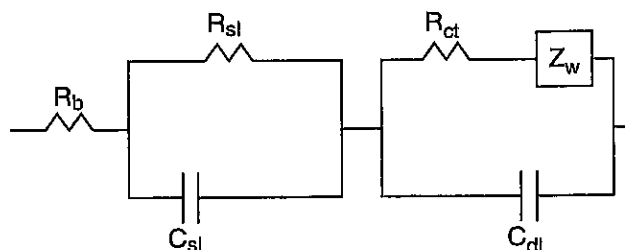


Figure 2. Equivalent circuit for the surface layer model.

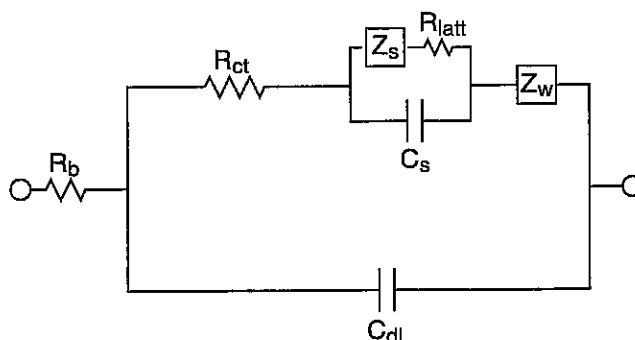


Figure 3. Equivalent circuit for the adatom model.

Inspection of the best fit values showed that Z_s , the surface diffusion impedance, had a value of zero; that is, this process is fast and is not rate-limiting at any frequency. This suggests that the distance between the site of adsorption and the site of intercalation is very short. It was also found that the rate determining step was the incorporation of the adion into the lattice (R_{latt} was several times larger than R_{ct} , the resistance for the adsorption/electron transfer reaction).

Reference

- 1) B.G. Sibernagel and M.S. Whittingham, *J. Chem. Phys.* 64 (1976) 3670-3677.

