

## The $\text{Li}_x\text{TiS}_2|\text{Li}_{(1-x)}\text{CoO}_2$ solid-state rocking chair battery

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### Abstract

The present paper describes the fabrication and characterization of a novel type of a solid-state, thin-layer lithium rocking chair battery. The battery utilizes titanium disulfide,  $\text{TiS}_2$ , as the negative 'lithium sink' electrode, lithium cobalt dioxide,  $\text{Li}_x\text{CoO}_2$ , as the positive 'lithium source' electrode, and a composite lithium ion-conducting polymer membrane as the electrolyte. Our initial studies on this novel system involved characterization of the charge/discharge behaviour and a.c. impedance responses.

### Introduction

While various types of primary lithium batteries have reached the commercial stage, there are no examples of a rechargeable Li battery which is commercially available on a large production scale. One of the main reasons for the failure of rechargeable Li batteries to reach this commercial production stage is the reactivity of the alkali metal resulting in significant degradation upon cycling and poor capacity retention upon storage [1]. Consequently, the replacement of Li by alternative non-metallic anode materials capable of storing and exchanging large quantities of Li ions has been the subject of a number of recent studies [2-6]. The Li concentration cells described in these recent studies are referred to as lithium rocking chair batteries.

The rocking chair batteries under present development use liquid organic electrolyte solutions and thus suffer from solvent decomposition upon cycling [1]. In the present work we describe the fabrication and characterization of a new type of rocking chair battery where the liquid electrolyte is replaced by a solid, thin-layer Li ion-conducting polymer membrane formed by the combination of poly(ethylene oxide), PEO, with lithium perchlorate,  $\text{LiClO}_4$ , and the addition of 10 mass%  $\gamma\text{-LiAlO}_2$  powder [7].

### Experimental

The preparation of the  $(\text{PEO})_8\text{-LiClO}_4$  composite polymer electrolyte containing 10 mass%  $\gamma\text{-LiAlO}_2$  is described in detail in ref. 7. Briefly, appropriate quantities of

LiClO<sub>4</sub> (Fluka reagent grade) and PEO (BDH) to give an O:Li molar ratio of 8:1 were dissolved in HPLC-grade acetonitrile (Aldrich). After stirring, the appropriate amount of  $\gamma$ -LiAlO<sub>2</sub> powder (4  $\mu$ m partical size) was added to the solution. Upon complete homogenization, the mixture was cast onto a flat polytetrafluoroethylene (PTFE) sheet and covered to allow slow evaporation of the acetonitrile. With this procedure, 50–100  $\mu$ m thick polymer membranes were obtained which were free from powder agglomeration.

The electroactive Li-insertion compound electrodes, namely titanium disulfide (TiS<sub>2</sub>) and lithium cobalt(III) oxide (LiCoO<sub>2</sub>), were prepared in the form of thin films deposited on aluminium foil which serves both as the electrode support and current collector. Thin films of TiS<sub>2</sub> were prepared by chemical vapour deposition onto the aluminium substrate, and the thin films of LiCoO<sub>2</sub> were prepared by a sol-gel method which involves thermal decomposition of the organometallic on an aluminium substrate [8].

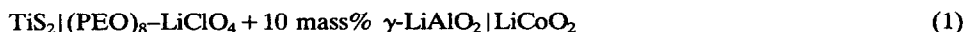
The solid-state thin-layer rocking chair cells were assembled in an argon-filled dry box (less than 10 ppm water content). The cells consisted of two 100  $\mu$ m polymer electrolyte membranes sandwiched between the negative (TiS<sub>2</sub>) and positive (LiCoO<sub>2</sub>) flag electrodes. Good interfacial contacts were obtained by pressing the sandwich between two glass plates. The cell was then sealed (TorrSeal<sup>®</sup>) and removed from the glove box for electrochemical testing.

Thermal control was accomplished by placing the cells in a Buchi Model T0-51 oven and equilibrating at 82 °C overnight. The cells were then cycled between 2.5 and 0.2 V at this temperature using a PAR model 273 potentiostat. All cells were cycled galvanostatically at a charge and discharge current density of 0.025 mA cm<sup>-2</sup>.

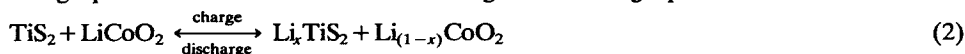
The characteristics of the electrochemical process were investigated by a.c. impedance spectroscopy over a frequency range of 10 mHz to 50 kHz using a Solartron 1255 frequency analyser and a Solartron 1286 electrochemical interface coupled to an IBM model 170 PC.

## Results and discussion

Rocking chair batteries are systems based on Li ion intercalating compounds acting both as negative and positive electrode materials. For the system investigated in the present study, TiS<sub>2</sub> is used as the 'lithium sink' negative electrode, and LiCoO<sub>2</sub> is the 'lithium source' positive electrode. The electrolyte is a composite Li<sup>+</sup>-conducting (PEO)<sub>8</sub>-LiClO<sub>4</sub> polymer membrane containing 10 mass%  $\gamma$ -LiAlO<sub>2</sub>. The cell can be represented by:



It should be noted that TiS<sub>2</sub>, which is one of the commonest cathodes in conventional Li batteries, is used here as the anode to accept Li<sup>+</sup> ions from LiCoO<sub>2</sub> during the charge process and to release them during the discharge process:



There are two main reasons for the selection of Li<sub>x</sub>TiS<sub>2</sub> as the negative electrode. One is related to its open layered structure which allows loose interactions with the guest Li ions: the intercalation of these ions within the S-Ti-S layers is accompanied by a modest free-energy change and, thus, by a limited voltage variation of around 0.7 V passing from  $x=0$  to  $x=1$  [9]. Therefore, the use of TiS<sub>2</sub> as the negative electrode

may limit voltage fluctuations upon cycling, this being one of the major problems experienced with common-design rocking chair batteries [6]. The second reason for selecting  $\text{Li}_x\text{TiS}_2$  as the preferred negative electrode is related to the fact that this compound intercalates Li at potentials about 2 V more negative than  $\text{LiCoO}_2$  and thus the combination of the two intercalating compounds results in reasonably high cell voltages. In addition, the cell voltage remains sufficiently low to preclude reduction and/or oxidation of the electrolyte. For polymer electrolytes including the present PEO-based polymer, the average stability window is at least 4.5 V versus  $\text{Li/Li}^+$  [10].

Other immediate advantages in using polymer electrolytes in rocking chair batteries are low cost, high reliability and ease of fabrication of thin-layer configurations such as bipolar cells [6]. Furthermore, the specific electrolyte selected in this work exhibits superior mechanical and transport properties to the simpler PEO- $\text{LiX}$  binary mixtures which allows one to lower the operating temperature from around 100 to around 80 °C.

The cell (1) which is assembled in the discharged state exhibits an open-circuit voltage (OCV) of 0.2 V at 82 °C. After charging at a constant current density of  $0.025 \text{ mA cm}^{-2}$  to a voltage limit of around 2.5 V, the cell assumed a charged state OCV of 2.1 V. The cell was then discharged at the same current density to a voltage cutoff level of 0.2 V, and the cycling regime repeated several times with the typical trend illustrated in Fig. 1.

The results indicate that the cell exhibits an excellent charge/discharge efficiency approaching 100%. However, the discharge curve shows a sloping trend suggesting that in the particular cell configuration adopted here, the polarization on discharge is somewhat higher than that on charge. To further investigate this phenomenon, a fully discharged cell was examined by a.c. impedance spectroscopy. Figure 2 illustrates the result: the impedance response clearly reveals that the kinetics of the electrochemical process is controlled by diffusion which appears to be associated with the insertion/

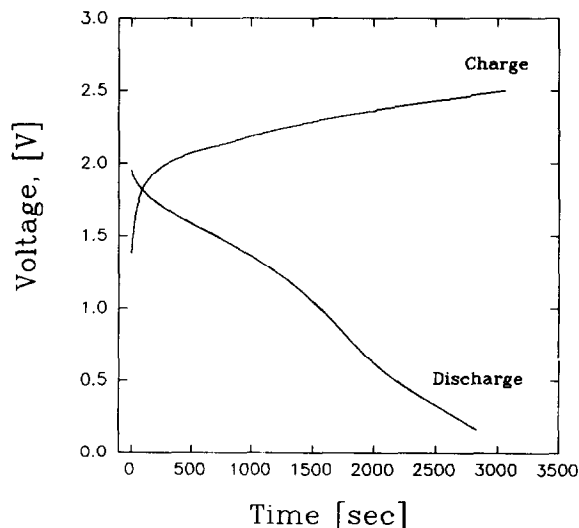


Fig. 1. Typical charge/discharge cycle at 82 °C of the  $\text{Li}_x\text{TiS}_2|(\text{PEO})_8\text{-LiClO}_4 + 10 \text{ mass\% } \gamma\text{-LiAlO}_2|\text{Li}_{(1-x)}\text{CoO}_2$  cell: charge/discharge current density =  $0.025 \text{ mA cm}^{-2}$ .

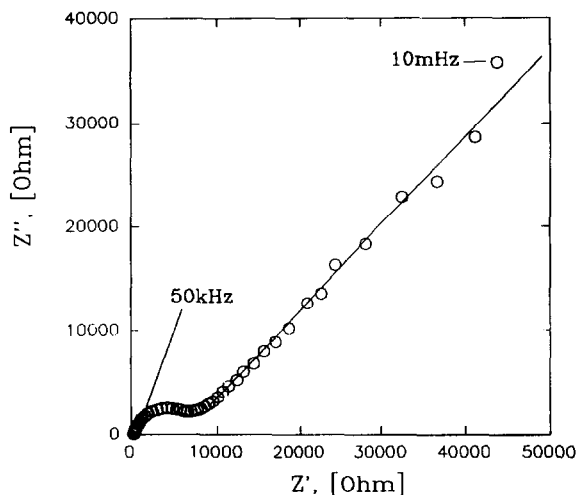


Fig. 2. Impedance response of the  $\text{Li}_x\text{TiS}_2|(\text{PEO})_8\text{-LiClO}_4 + 10 \text{ mass\% } \gamma\text{-LiAlO}_2|\text{Li}_{(1-x)}\text{CoO}_2$  cell at  $82^\circ\text{C}$  in its fully discharged state. The  $45^\circ$  Warburg line was constructed using a fitting program. Frequency range is 10 mHz to 50 kHz.

deinsertion of  $\text{Li}^+$  ions within the host electrode compounds. This in turn suggests that improvements in the discharge behaviour of this new type of solid-state rocking chair battery may be achieved by optimization of the cell design, the morphology and the reciprocal composition of the electrode materials. These investigations are presently in progress in our laboratories.

### Acknowledgements

One of the authors (B.S.) is grateful to the US Army European Research Office in London, UK, for providing support for a visit to Fort Monmouth for discussions on this collaborative research.

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