

CYCLING BEHAVIOUR OF THE POLYPYRROLE-POLYETHYLENE OXIDE COMPOSITE ELECTRODE

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Summary

An all-solid-state battery utilizing a thin, composite polypyrrole-polyethylene oxide positive electrode, solid polymeric electrolyte, and a lithium negative electrode was constructed and its cycling behaviour evaluated. Hundreds of cycles were reached before the coulombic capacity decreased to 60% of its original value. The gravimetric energy density of the composite electrode was estimated to be 55 Wh kg^{-1} . The disadvantage of the battery is poor charge retention, and high-rate performance is limited by the diffusion of anions in the polypyrrole particles.

Introduction

There is widespread international interest in the development of all-solid-state batteries exploiting polymeric electrolyte materials. A solid state, rechargeable lithium battery is being developed, for vehicular traction applications and other storage batteries, as a collaborative Anglo-Danish project [1]. The cell incorporates a lithium or lithium-based negative electrode and a positive electrode containing a vanadium oxide (or other inorganic insertion compounds) as the active material. The electrolyte is a complex formed between poly(ethylene oxide) (PEO) and the lithium salt, e.g., lithium trifluoromethanesulphonate, LiCF_3SO_3 [2]. A similar battery structure is under French-Canadian development [3].

Since the first report of organic electroactive polymers being used in secondary batteries [4], these materials have been extensively studied in different laboratories [5]. Polyacetylene is the material about which most data have been published, but other polymers such as polyparaphenylene

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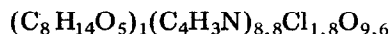
[6], polypyrrole [7] and polythiophene [8] are also being studied. Some of the major problems found in these systems are those of poor chemical stability under extended cycling when the organic electrode material is combined with a liquid electrolyte [9].

Such difficulties may be solved by the use of solid polymer electrolytes because they are inert [10, 11]. The battery with a lithium or lithium-based negative electrode, solid polymer electrolyte, and positive electrode containing organic electroactive polymer should, therefore, combine the advantages of both battery concepts. Studies of the application of PEO in combination with polyacetylene have been reported by Chiang [12] but poor interpenetration of the two classes of polymer limited the performance of this structure.

As soluble electroactive polymers are now available [13], we succeeded in developing a new class of composite electrode material based on both electroactive polymers and polymeric solid electrolyte [14]. The composite electrode, with increased interfacial area between the two phases, and with both electronic and ionic conductivity, shows enhanced coulombic capacity as compared with an electrode composed only of electroactive material. Because of the promising electrochemical properties of the polymeric composite electrode we decided to investigate the material further in order to evaluate the cycle life of our new electrode.

Experimental

Colloidal solutions of polypyrrole (PPy) were prepared by chemically oxidizing pyrrole monomer with FeCl_3 in aqueous solutions of methylcellulose or hydroxypropylcellulose by the method described elsewhere [13, 14]. Chemical analysis of the polypyrrole/methylcellulose starting material gave the following composition:



The same hydroxypropylcellulose-polypyrrole ratio was found for the hydroxypropylcellulose-based starting material. The $\text{PPy-P}(\text{EO})_8 \cdot \text{LiClO}_4$ composite electrode was prepared by mixing aqueous solutions of both components [14]. The resulting mixture was used to form films by casting onto stainless steel disks (which served as current collectors). The water was allowed to evaporate in the atmosphere at room temperature. The samples were then transferred to a glove box with a dry argon atmosphere and left to dry overnight (at least).

The polyethylene oxide (BDH Chemicals, M. W. = 600 000) based solid electrolyte ($\text{P}(\text{EO})_8 \cdot \text{LiClO}_4$) was prepared inside the glove box by casting the dry 1 vol.% solution of the solid electrolyte in acetonitrile onto a PTFE plate. The solvent was allowed to evaporate in the glove box atmosphere at 25 °C. The resulting film, about 100 μm thick, was dried for at least one week in the dry argon environment of the glove box.

All electrochemical measurements were performed using hermetically sealed, two-electrode cells (modelling the button cell structure) as shown in Fig. 1. Freshly scraped lithium metal was pressed into a stainless steel die. The circular lithium surface was covered with two sheets of the solid electrolyte, and the composite PPy-PEO electrode (geometric area 1.77 cm^2) on a stainless steel supporting disk was attached to the top of the structure. The electrode assembly, spring-loaded to *ca.* 1 kg cm^{-2} , was hermetically sealed with PTFE foil and taken out of the glove box for the electrochemical measurements.

All measurements were done at 85°C . The $E-t$ and $E-I$ curves were recorded with an X-Y recorder and the data were stored simultaneously in a computer for analysis.

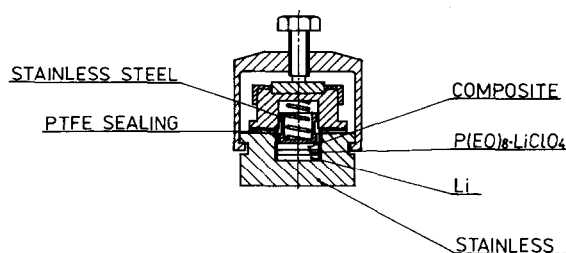


Fig. 1. The structure of the $\text{Li}/\text{P}(\text{EO})_8 \cdot \text{LiClO}_4/\text{PPy} + \text{P}(\text{EO})_8 \cdot \text{LiClO}_4$ composite cell.

Results and discussion

From our first experiments [14] with PPy-PEO composites used as positive electrodes in solid-state lithium cells we selected galvanostatic cycling between 2.20 and 3.10 V (*versus* Li/Li^+) as the most suitable method for the evaluation of the cycle life parameters.

The galvanostatic charge and discharge capacity of a typical thin PPy-P(EO) $_8$ ·LiClO $_4$ composite electrode is plotted in Fig. 2 as a function of the cycle number. These results are promising with 60% of the original coulombic capacity remaining after 170 cycles. The coulombic efficiency is very good (mean value 96%, minimum 91.7%, maximum 99.1%), and the energy efficiency of 80 - 85% is acceptable. The mean discharge voltage of our composite material is about 2.45 V (*versus* Li/Li^+) with discharge/charge curves without steps or plateaux (Fig. 3). The cyclic voltammetric curves are also smooth with no well-developed peaks (Fig. 4). This behaviour is in accordance with the generally accepted insertion model* of the doping/undoping (*i.e.*, charging/discharging) of the electroactive polymer electrode [5].

*Electrode reaction: $(\text{Py})_x + xy\text{A}^- \rightleftharpoons (\text{Py}^{\text{y}+} \cdot \text{A}_y^-)_x + xye^-$; $\text{A} = \text{ClO}_4^-$ or Cl^- .

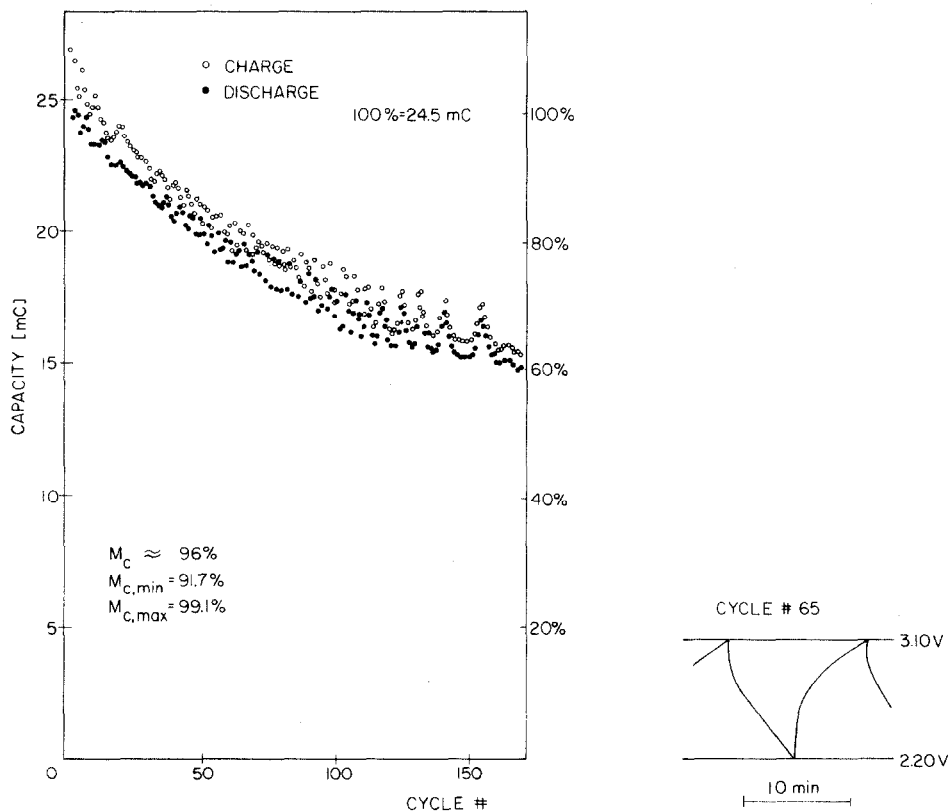


Fig. 2. Dependence of the discharge (●) and charge (○) capacity of the hydroxypropylcellulose-based PPy-P(EO)₈-LiClO₄ composite electrode on the cycle number. Composite with 50% PEO; galvanostatic cycling $\pm 50 \mu\text{A}$ between 2.20 and 3.10 V (*vs.* Li/Li⁺); temperature 85 °C.

Fig. 3. Typical cycling profile of the composite electrode. Cycling conditions as in Fig. 2.

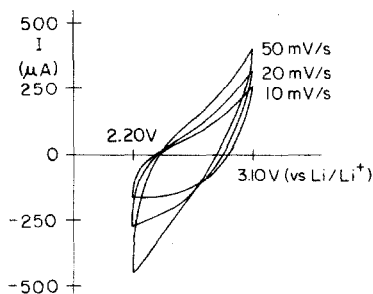


Fig. 4. Typical cyclic voltammograms of the hydroxypropylcellulose-based PPy-P(EO)₈-LiClO₄ composite electrode. Temperature 85 °C, electrode area 1.77 cm², sweep rates 50, 20, and 10 mV s⁻¹.

The battery under investigation is diffusion-limited, as indicated by the linear dependence of both anodic and cathodic charges (from cyclic voltammetry) on the reciprocal square root of the sweep rate (Fig. 5). We believe that the diffusion limitation is connected with the movement of anions in the PPy particles because the diffusion coefficient for this case is around $10^{-12} \text{ cm}^2 \text{ s}^{-1}$ [14], the diffusion in PEO-based solid electrolyte should be fast enough (the diffusion coefficient of inorganic species in PEO is $10^{-7} \text{ cm}^2 \text{ s}^{-1}$ [15]). There are negligible ohmic and activation overpotentials because when the current ($50 \mu\text{A}$) is interrupted the change in the cell voltage is only 10 - 20 mV during the first second after interruption.

In order to achieve many cycles in a relatively short time we prepared some very thin electrodes with a capacity of about 3 mC only. A typical result is shown in Fig. 6 where discharge capacity is plotted as a function of the cycle number. Again, the composite PPy-PEO electrode proved to be very stable from the point of view of the cycle life; after 700 cycles the experiment was interrupted without any significant loss of coulombic capacity.

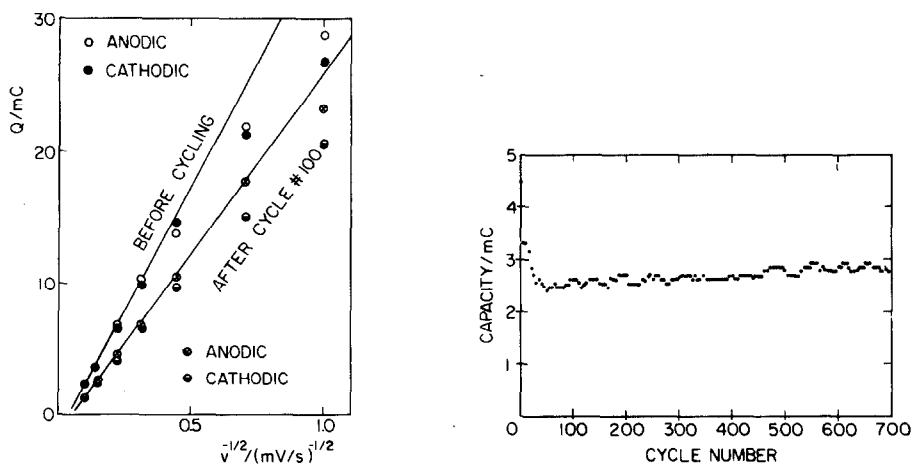


Fig. 5. Dependence of the anodic and cathodic charges, Q , from cyclic voltammetry of the composite electrode, on the reciprocal square root of sweep rate (experimental conditions as in Fig. 4). Data were taken before galvanostatic cycling and after 100 galvanostatic cycles between 2.20 and 3.10 V using $\pm 50 \mu\text{A}$.

Fig. 6. Dependence of the discharge capacity of the hydroxypropylcellulose-based PPy-P(EO)₈-LiClO₄ thin composite electrode on the cycle number. Composite with 50% PEO; galvanostatic cycling $\pm 50 \mu\text{A}$ between 2.20 and 3.10 V (*vs.* Li/Li⁺); temperature 85 °C.

The coulombic capacity of a thick composite electrode is plotted in Fig. 7 as a function of the cycle number. In this case the thickness of the electrode (about 20 μm) is similar to the thickness of practical positive electrodes for solid state batteries with polymeric electrolyte [1]. There is

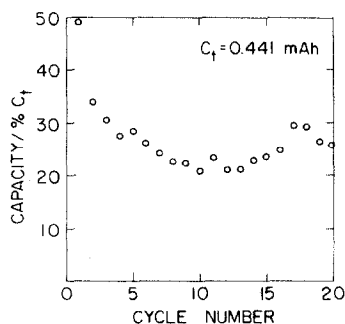


Fig. 7. Dependence of the discharge capacity of the methylcellulose-based PPy-P(EO)₈-LiClO₄ thick composite electrode on the cycle number. Composite with 30% PEO; galvanostatic cycling $\pm 50 \mu\text{A}$ between 2.20 and 3.10 V (*vs.* Li/Li⁺); temperature 85 °C.

no significant difference between thin and thick electrode performances. We point out that there is still the possibility — not yet explored — of optimizing the composition of the electrode material and improving the performance characteristics of thick electrodes.

The maximum coulombic capacity of the PPy electrode is around 0.25 electrons per pyrrole ring [16]. (This value is used in this paper as a theoretical capacity of the PPy-PEO composite electrode, C_t .) Using the loading $50 \mu\text{A}$ (*i.e.*, a current density of about $30 \mu\text{A cm}^{-2}$) the utilization of PPy in our cell is around 25% C_t . When the current density is decreased, the utilization of PPy is enhanced (Table 1). Based on the mean discharge voltage of 2.45 V and 36% utilization of the polypyrrole we calculated the gravimetric energy density of the composite electrode material to be 55 W h kg^{-1} . (The

TABLE 1

Dependence of the discharge capacity of the methylcellulose-based PPy-P(EO)₈-LiClO₄ composite electrodes on the discharge current

$I_{\text{charge, disch.}}$ (μA)	30% PEO		Without PEO	
	Q_D (mC)	$\frac{Q_D}{Q_C}$ (%)	Q_D (mC)	$\frac{Q_D}{Q_C}$ (%)
20	36.0	81	5.2	73
50	25.0	91	5.5	96
100	16.1	94	2.9	94
200	10.6	96	2.5	86
500	5.9	92	2.4	80

Average data from 5 galvanostatic cycles between 2.20 and 3.10 V (*vs.* Li/Li⁺); temperature 85 °C; after 30 preliminary cycles with $\pm 50 \mu\text{A}$. Theoretical capacity $C_t = 100 \text{ mC}$.

energy density during the first few cycles is higher, but we used the data after 30 preliminary galvanostatic cycles when the performance of the electrode had stabilized.) The difference between the first and the 30th cycle could be explained by the fact that $\text{PPy}^{y+} \cdot \text{Cl}_y^-$ is combined with $\text{P(EO)}_8 \cdot \text{LiClO}_4$ leading to disequilibrium between Cl^- and ClO_4^- ions in the system. The self-discharge of our model 'coin' cell is rapid. In the case of a thick pellet we observed a 50% loss of charge under open-circuit after 4 h, and total self-discharge after one day. We believe that self-discharge can be avoided by judicious chemistry, possibly using high purity materials (Varta AG reported a PPy battery with only a 1% loss of charge/day [17]). The other possible explanation is diffusion of PPy in the soft $\text{P(EO)}_8 \cdot \text{LiClO}_4$ layer. Experiments to find the reason for the high self-discharge rate are in progress.

Conclusion

We have demonstrated a promising cycle life of hundreds of galvanostatic cycles for the composite polypyrrole-polyethylene oxide electrode used with a lithium counter-electrode and solid polymeric electrolyte in a solid-state, rechargeable battery. The gravimetric energy density, 55 W h kg^{-1} (based on the weight of the composite material), is rather low but this parameter was not optimized. The method of preparation of the composite electrode is very simple and, with improved self-discharge characteristics, the composite polymeric electrode material could be a good alternative to inorganic compound-based positive electrodes for all-solid-state cells.

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