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Plastic power sources*

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Lithium ion polymer batteries and laminated solid-state redox supercapacitors, formed by placing a highly conducting gel-type membrane electrolyte between a graphite film and a composite cathode film and between a poly(pyrrole)–poly(aniline) electrode combination, respectively, have been fabricated and tested. The preliminary results are encouraging in suggesting that these plastic power sources may be particularly advantageous for mobile electronic products and for zero emission electric vehicles.

Keywords: *batteries*, *lithium-ion*, *polymer electrolytes*, *plastic batteries*, *supercapacitors*

1. Introduction

The growing market for mobile electronic products and the stringent demand for environmentally compatible vehicles has motivated research on the development of electrochemical power sources characterized by high energy and/or high power density, good cyclability, reliability and safety [1]. A recent breakthrough has been the commercialization of rechargeable lithium batteries, the so called lithium-ion batteries [2], which are now produced at a million units per month for the '3Cs' (i.e., cellular telephones, portable computers and camcorders) market. Another important innovation in the field is the development of redox supercapacitors, namely of high-power devices designed for combination with high-energy batteries in order to assure well-balanced electric vehicle operation [3]. In this combination, the former provides the peak needs for the vehicle acceleration while the latter assures its long range running.

Most of the lithium ion battery and supercapacitor R&D projects are focused on the fabrication of prototypes using liquid electrolytes. An important step forward in this technology would be the replacement of the liquid electrolyte with an ionic membrane to produce devices having a full plastic configuration. This is an interesting concept, since it provides the prospect of a favourable combination of the high energy and the long life, typical of lithium or of lithium-ion cells, with the reliability and processability, typical of polymer-based, all-solid-state structures. The practical development of this concept requires the availability of polymer electrolytes having ionic conductivities approaching those of the liquid solutions and a good compatibility with the electrode materials. Gel-type polymer membranes, formed by trapping liquid solutions (e.g., a solution of a lithium salt in organic solvent mixtures) in a polymer network (e.g., a poly(acrylonitrile), PAN or poly(methylmethacrylate)PMMA, matrix) [4–6] appear to be suitable for this purpose. To confirm this expectation, we have fabricated and tested plastic prototypes of lithium ion cells and supercapacitors. The results are reported in this work.

2. Experimental details

The gel-type, electrolyte membranes were prepared by immobilizing ethylene carbonate–propylene carbonate, EC–PC, or ethylene carbonate–dimethylcarbonate, EC–DMC, solutions of $LiClO_4$ in a PAN or in a PMMA matrix. The details of this procedure were reported in previous papers [7, 8]. Dimensionally stable membranes, of thickness ranging between 100 and 200 μm, were typically obtained. For reasons of simplicity, the membranes are hereafter indicated by writing in sequence the lithium salt, the liquid solvent mixture and the immobilizing polymer, that is, with the notations $LiClO_4$–EC–PC–PAN, $LiClO_4$–EC–DMC–PAN or $LiClO_4$–EC–PC–PMMA. The composition of the membranes are (in molar ratio) 8 : 38 : 33 : 21 and 4.5 : 46.5 : 19 : 30, respectively.

The lithium ion anode film electrodes were prepared by spreading on a copper foil current collector a mixture of graphite (Lonza KS 44) and a poly(vinyl chloride)–poly(tetra ethylene fluoride) PVC–PTFE binder. The cathode film was similarly formed by spreading a mixture of the active component (a Cr-stabilized lithium manganese spinel, of formal $LiCr_yMn_{2-y}O_4$ composition (samples were kindly provided by Prof. M. Wakihara of Tokyo Institute of Technology, Japan and by Dr R. Howard of Covalent Associates, USA) carbon and the PVC–PTFE binder on an aluminium foil current collector [9].

The poly(pyrrole), pPy, electrodes and the poly(aniline) pAni, electrodes were galvanostatically synthesized on steel net current collectors from

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* This paper is dedicated to the memory of Professor Giuseppe Bianchi.

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aqueous solutions containing the monomers and the supporting electrolyte, that is, lithium dodecylsulfate (LiDS) in the case of pPy and sulphuric acid and sodium sulphate in the case of pAni. Details of the syntheses have been reported in previous papers [10, 11]. Both the polymer electrodes were cleaned by voltammetric scans in cells using the $\mathrm{LiClO_4}$, EC–PC liquid organic solutions.

The lithium ion plastic battery prototypes were assembled in an environmentally controlled dry box by pressing into appropriate coin-type containers a sequence formed by a graphite anode, the electrolyte membrane and a composite film cathode [9]. The cells were sealed and tested using Maccor cycling equipment.

The plastic, laminated supercapacitor prototypes were fabricated by placing a $\mathrm{LiClO_4}$–EC–PC–PMMA electrolyte membrane between the pPy and pAni film electrodes supported by two steel net current collectors. A third, lithium metal electrode was placed laterally to act alternatively as a counter (for single electrode potential control) or as a reference (for electrochemical studies) electrode [11]. The two polymer electrodes were activated by voltammetric scans and, subsequently, charged potentiostatically. The supercapacitor performance was investigated by cyclic voltammetry and by galvanostatic discharge curves using an AMEL 551 potentiostat coupled with an Amel 567 function generator. A Solartron 1250 frequency response analyser was used for the electrochemical impedance studies.

3. Results and discussion

3.1. *Plastic lithium ion batteries (PLIBs)*

The replacement of the liquid electrolyte with a polymer electrolyte in a lithium ion battery is not a straightforward operation [12]. The challenging requirement for the success is to achieve good compatibility between the electrode and the electrolyte components, with particular concern for the negative, carbon electrode side. The major problem is to assure a full wettability throughout the entire electrode bulk, a process which is naturally achieved when the electrode is immersed into a liquid solution but which must be activated or promoted when the same electrolyte is confined within a polymer matrix.

A successful approach toward the development of PLIBs of practical relevance has been reported by the Bellcore Laboratory in the United States with the use of a membrane separator formed as a copolymer of vinylidene fluoride and hexafluoropropylene (PVDF–HFP), which is capable of absorbing large quantities of liquid electrolyte [13, 14].

We have attempted to design an alternative process involving the direct lamination of the battery components without intermediate liquid extraction–activation steps. For this purpose we have selected electrolyte membranes which, although being macroscopically stable, allow a certain degree of release of the liquid solution component. A good example is provided by gel type membranes using PAN as the polymer matrix, which may be formed with an excess of liquid [7]. The release of some of this excess wets the membrane surface and this is expected to favour proper interlayer contact with the graphite electrode by the filling of its micropores.

To test the validity of this expectation, we have evaluated the electrochemical response of a graphite film electrode in a $\mathrm{LiClO_4}$–EC–DMC–PAN electrolyte cell. The test was run by following the lithium intercalation process using a lithium metal counter electrode, that is, by monitoring the potential of the carbon electrode during the lithium intercalation–deintercalation processes:

$$x\mathrm{Li}^+ + 6\,\mathrm{C} \longleftrightarrow \mathrm{Li}_x\mathrm{C}_6$$

Figure 1 illustrates the result reported in terms of a voltage–capacity curve obtained during the first charge (intercalation)–discharge (deintercalation) cycle. The response approaches that expected in liquid electrolyte cells: the voltage profile of the charge process decreases along a series of distinguishable plateaux which correspond to the progressive formation of staged phases [2]. A similar trend is reproduced in discharge, although with a decay in capacity. This is also expected, since the formal excess in capacity during the initial charging cycles may be explained by side reactions involving the decomposition of the electrolyte with the formation of a passivation film on the graphite electrode surface [2]. The occurrence of this layer, which is electronically insulating but ionically conducting, was also demonstrated by impedance studies carried out on the graphite anode at various cycling stages in the $\mathrm{LiClO_4}$–EC–DMC–PAN electrolyte cell. The impedance response of a graphite electrode after the eight full charge cycle showed a large expansion of the middle frequency semicircle (to indicate an increase in the interfacial resistance, as that induced by the formation of a passivation layer) and a low frequency trend passing from a 90° capacitance line to a 45° spike (to suggest mass transfer controlled kinetics, as those expected by the diffusion of the lithium ions across the layer).

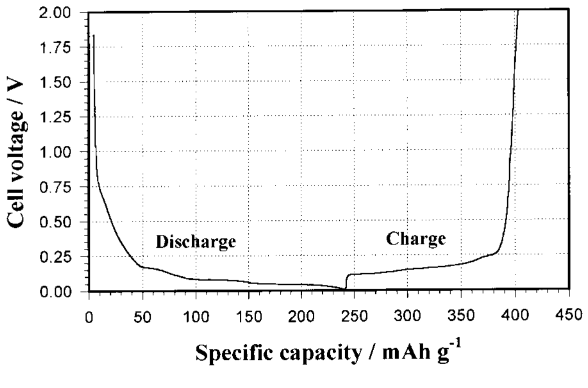

Fig. 1. Voltage profile of the charge–discharge process of a $\mathrm{Li}_x\mathrm{C}_6$ graphite film electrode in a $\mathrm{LiClO_4}$–EC–DMC–PAN electrolyte cell. Counter electrode: lithium metal. Cycling rate: $0.03\,\mathrm{mA\,cm^{-2}}$. Room temperature.

The formation of the passivation layer is typical of carbonaceous electrodes in all types of electrolytes. In contrast with the case of the lithium metal electrode where it may induce safety problems [12], in carbonaceous electrodes this phenomenon is beneficial for assuring proper cyclability. Accordingly, also in the case of the cell here tested, the charge–discharge efficiency of the graphite film electrode approaches 100% after the second cycle and remains at this value for all the subsequent cycling.

Very similar results have been obtained using other types of PAN-based membranes, such as the $LiClO_4$–EC–PC–PAN case. On average, the graphite electrodes can be cycled in these polymer electrolyte membranes with a reversible capacity ranging about 100 mA h g^{-1}. This value is less than that usually obtained in liquid electrolytes (approaching 370 mA h g^{-1}). However, there are convincing indications that the capacity delivery can be enhanced by the optimization of electrode design and configuration and thus, that the PAN-based membranes are indeed effective polymer electrolytes for cycling graphite electrodes.

We have then extended the test of the compatibility of these membranes to the other electrodic side, namely to the lithium metal oxide cathode. Among the known lithium ion oxide cathodes, $LiMn_2O_4$ is a very desirable choice since it is nontoxic and much less expensive than its counterparts. However, to assure good capacity retention upon cycling it is important to stabilise the spinel structure, for instance by a partial substitution of Mn(III) with M(III) admetals [15]. Promising cycling behaviour has been reported for chromium substituted spinels [16, 17] and we selected this type of improved cathode materials for testing in view of PLIB development.

As in the case of the graphite electrodes, we first evaluated the electrochemical response of a Li–Cr-manganese oxide film electrode in a $LiClO_4$–EC–PC–PAN electrolyte cell. Again the test was run by following the lithium intercalation process using a lithium metal counter electrode, that is, by monitoring the potential of the spinel electrode during the lithium deintercalation–intercalation process:

$$LiCr_yMn_{2-y}O_4 \longleftrightarrow xLi^+ + Li_{1-x}Cr_yMn_{2-y}O_4$$

Figure 2, which illustrates the result, reveals that the voltage profile and the cycling capacity (i.e., about 130 mA h g^{-1}) match those expected for this cathode material in liquid electrolytes [2]. Furthermore, the small voltage drop in passing from charge to discharge confirms that the PAN-based electrolyte membrane fulfils satisfactorily the desired requirement of a low-resistive polymer electrolyte. Finally, the well defined and reproducible shapes of the charge and discharge curves suggest that the cycling process is fast, reversible and, most importantly, that it does not induce drastic modifications in the spinel cathode structure. Indeed, the Cr-modified spinel cathode can be effectively cycled with high charge–discharge efficiency and with a capacity delivery exceeding 60 mA h g^{-1}after 1100 cycles [9].

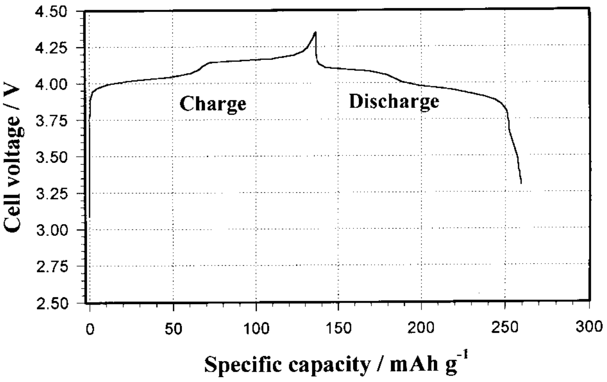

Fig. 2. Voltage profile of the 1st charge–discharge process of a $LiCr_yMn_{2-y}O_4$ film electrode in a $LiClO_4$–EC–PC–PAN electrolyte cell. Counter electrode: lithium metal. Cycling rate: 0.1 mA cm^{-2}. Room temperature.

Once having ascertained the compatibility of the membrane electrolyte with both side electrodes, we extended the investigation to complete PLIB prototypes. These were fabricated by simply contacting in sequence a graphite anode film, a $LiClO_4$–EC–PC–PAN electrolyte membrane and a $LiCr_yMn_{2-y}O_4$ composite film cathode. The basic electrochemical process is the cycling transfer of lithium ions from the manganese spinel electrode to the graphite electrode:

$$6\ C + LiCr_yMn_{2-y}O_4 \longleftrightarrow Li_xC_6 + Li_{1-x}Cr_yMn_{2-y}O_4$$

Figure 3 shows the voltage profile of the initial two charge-discharge cycles of the PLIB prototype plotted against the capacity of the lithiated-graphite anode. The large irreversible capacity shown in the first cycle is related to the above discussed passivation phenomena occurring at the anode. As expected from the above illustrated single electrode responses, the charge–discharge efficiency of the PLIB tends to approach 100% after the initial few cycles and to maintain this value for a prolonged number of cycles. This is further demonstrated by Fig. 4 which illus-

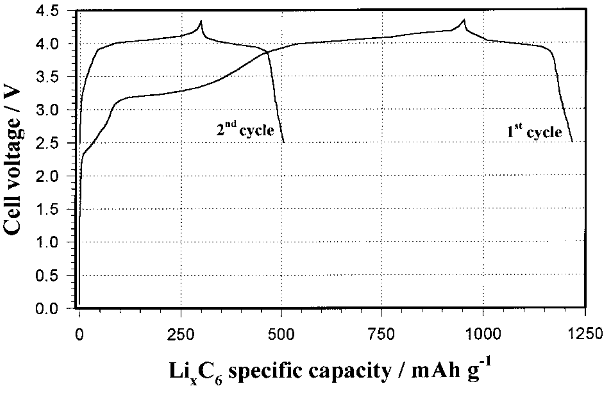

Fig. 3. Voltage profile of the first and second charge–discharge cycles of the C/$LiClO_4$–EC–PC–PAN/$LiCr_yMn_{2-y}O_4$ plastic coin type lithium ion battery. Room temperature. Cycling rate: 0.03 mA cm^{-1}.

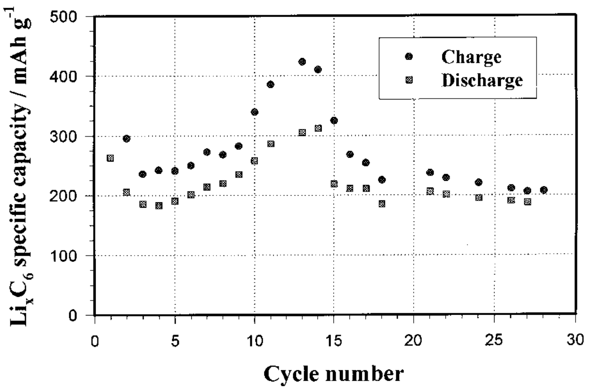

Fig. 4. Cyclability of the C/$LiClO_4$–EC–PC–PAN/$LiCr_yMn_{2-y}O_4$ plastic coin type lithium ion battery. Room temperature. Cycling rate: 0.03 mA cm^{-1}.

trates the cycling behaviour of the PLIB reported in terms of capacity of the lithiated-graphite anode versus cycle number. Some fluctuations, probably due to initial activation of the graphite electrode, are observed; however, the average value of the delivered capacity (i.e., 200 mA h g^{-1}) is promising in suggesting that the PAN-based gel-type ionic membranes are suitable for the fabrication of plastic lithium ion batteries, namely, of new-design power sources which may be particularly advantageous for mobile electronic products.

Another development in the area of this new type of devices which has been performed in our laboratory concerns the use of a very low cost family of cathode materials, i.e. polymers such as pPy or pAni. These materials can be used in replacement of lithium metal oxides (e.g., $LiCoO_2$, $LiNiO_2$ or the same lithium manganese spinels above discussed) for the fabrication of new types of PLIBs. A typical structure of these batteries may involve the following sequence:

$$\mathrm{C/LiClO_4\text{–}EC\text{–}PC\text{–}PMMA/pPy}$$

Battery prototypes were fabricated by preparing the electrodes in the form of thin films backed on metallic substrates and separating them by the polymer electrolyte membrane. In this case, the pPy and the graphite electrodes were preactivated by a few cycles against a lithium electrode in a liquid electrolyte cell before combining them in the final cell structure.

The charge–discharge process implies the double insertion and the extraction of the Li^+ ions at the graphite anode and at the poly(pyrrole) cathode, respectively:

$$6\,\mathrm{C} + [\text{–}(\mathrm{C_4H_3N})_y(\mathrm{DS})\mathrm{Li} \longleftrightarrow \mathrm{Li}_x\mathrm{C}_6 + [\text{–}(\mathrm{C_4H_3N})\text{–}]_y(\mathrm{DS})\mathrm{Li}_{1-x}$$

where y is the number of Py monomeric units corresponding to one positive doping charge [18] and x is the lithium intercalation level in the graphite. The process is accompanied by the typical voltage profiles illustrated in Fig. 5.

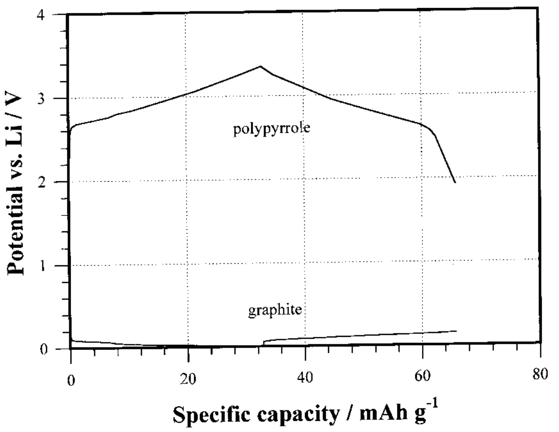

Fig. 5. Voltage profiles of the initial charge–discharge cycles of the graphite and of the poly(pyrrole) electrodes in the C/$LiClO_4$–EC–PC–PMMA/pPy(DS) plastic lithium ion battery. Room temperature. Cycling rate: 0.022 mA cm^{-1}.

Figure 6, which illustrates the cycling behaviour, shows that this PLB is indeed characterized by a good performance and, that it may be of practical interest [10]. The main advantages are in the type of electrode materials which are of low cost and compatible with the environment. Another favourable aspect is that, if properly prepared, the battery is capable of delivering reasonably high power pulses. Drawbacks in respect to the C/$LiMn_2O_4$ PLIBs are the lower capacity and, the lower energy density.

3.2. *Plastic redox supercapacitors (PRSCs)*

Two types of supercapacitors are currently proposed as complementary high-power devices in battery-operated vehicles, namely, the ‘double layer capacitors’ based on carbon electrodes and aqueous, generally acidic electrolytes [3] and the ‘redox capacitors’ using either noble metal (e.g., ruthenium) oxide electrodes [19] or polymer electrodes in nonaqueous electrolytes [20]. The first type, although being the closest to commercialization, suffers from relatively low capacitance. The development of the redox type using ruthenium oxide electrodes is subject to high cost. Thus, interest is currently focused on redox capaci-

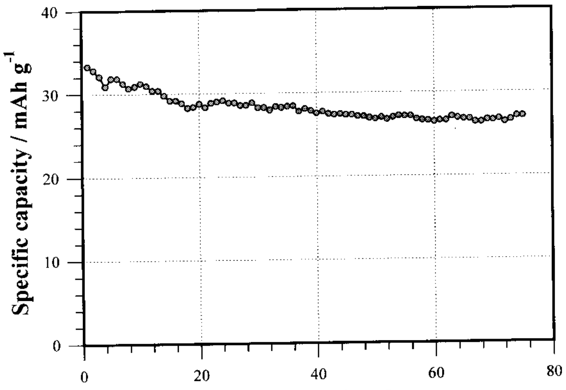

Fig. 6. Cyclability of the C/$LiClO_4$–EC–PC–PMMA/pPy(DS) plastic lithium ion battery. Room temperature. Cycling rate: 0.022 mA cm^{-1}.

tors using polymer electrodes; in fact they are not expensive, may be easily prepared in the form of extended surface thin films and can store charge throughout their entire volume [20].

The operation of these capacitors has been described in a previous paper [21]. Basically, the charge–discharge process of the device involves a fast and reversible electrochemical doping–undoping reaction [18] which may be exploited with two electrodes based on the same polymer (symmetric capacitors) or on polymers of different type (asymmetric capacitors).

Very few attempts to replace the liquid with a polymer gel electrolyte have been so far successfully reported for all types of supercapacitors. The fabrication and testing of double layer capacitors using gel electrolytes have been reported by Matsuda and coworkers [22] and by Osaka and coworkers [23], while plastic-like redox supercapacitor prototypes have been described by Mastragostino and coworkers [24]. In our laboratory we have extended the use of those gel-type electrolyte membranes which have been proved successful for PLIBs to the fabrication of plastic redox supercapacitors (PRSCs). We have considered asymmetric systems formed by the combination of two different polymer electrodes, i.e. pPy and pAni, separated by a $LiClO_4$–EC–PC–PMMA membrane [11]. In the fully charge condition, the pPy electrode is in its moderate p-doped state [18] while the pAni electrode is in its high p-doped state, and the PRSC prototype assumes its maximum voltage of 1.2 V. The discharge process involves the transfer of charge from one electrode to the other, with consequent decay in voltage difference, which reaches zero in the fully discharged state. Figure 7 illustrates the galvanostatic discharge curves of the prototype. The response is promising, giving at 0.5 mA cm^{-2} rate a specific capacity of 25 F g^{-1} (referred to the to total electrode active mass only), that is a value approaching that offered by comparable prototypes using liquid electrolytes [11].

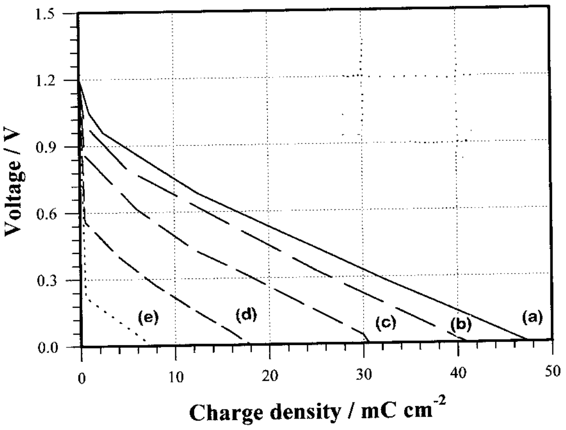

Fig. 7. Galvanostatic discharge curves at various current densities of the pPy/pAni plastic redox supercapacitor. Room temperature. Legend: (a) 0.5, (b) 1.0, (c) 2.0, (d) 2.0 and (e) 6.0 mA cm^{-2}.

4. Conclusion

The above results suggest that gel-type membranes are suitable electrolytes for the fabrication of new types of electrochemical power sources having a fully plastic configuration. Even under nonoptimized conditions, such as those used in this preliminary study, the plastic prototypes behave promisingly. This is further confirmed by the specific power–specific energy Ragone plots reported in Fig. 8. The Li-ion manganite prototypes reach energy density values up to 120 Wh kg^{-1}, that the same PLIB in the Li-ion polypyrrole version has very high specific power, while the PRSP (pAni/pPy) redox capacitor prototype offers a specific energy of 4 Wh kg^{-1} and a specific power of the order of 120 W kg^{-1}.

Acknowledgements

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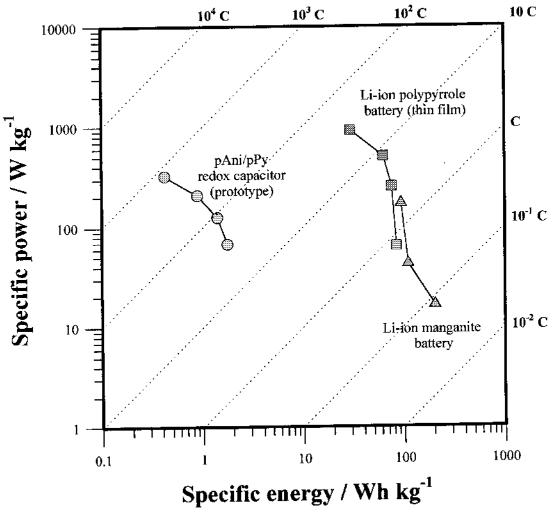

Fig. 8. Specific power versus specific energy (Ragone plots) for the plastic power source devices discussed in this work.

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