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A rechargeable battery of the type polyaniline/propylene carbonate–$LiClO_4$/Li–Al

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A secondary battery of the type polyaniline/propylene carbonate–$LiClO_4$/Li–Al is described. The polymer is made by aniline oxidation with ammonium persulphate in NH_4F, 2.3 HF as solvent. The discharge capacity of the polymer is $100\,Ah\,kg^{-1}$ at 25° C and $140\,Ah\,kg^{-1}$ at 40° C for current densities of $0.5\,mA\,cm^{-2}$ and for an amount of material giving a capacity of 10 mAh. The voltage in open circuit for the fully charged battery is 3.6 V. The average usable potential is 2.8–3 V. The energy density for the polymer lies between 280 and $420\,Wh\,kg^{-1}$. The ratio of the amounts of electricity in discharge and charge is one for several hundred deep cycles. The behaviour with regard to self discharge and to constant applied voltage (floating life) is excellent.

1. Introduction

The possible use of conducting polymers and, in particular, polyaniline, as active material in the positive electrode in rechargeable electrochemical generators (batteries) has already been described and its feasibility demonstrated [1–8]. Polyaniline is the preferred conducting polymer as it has a number of advantages over other conducting polymers. Its discharge capacity is greater than that of polypyrrole, for example, which is theoretically limited to $88\,Ah\,kg^{-1}$ in the presence of perchlorate [9]. The self discharge is better than that of polythiophene which is 25% after 3 days [10] and polyacetylene which reaches 35% after 12 h [10]. The Ni–Cd generator also presents a self discharge greater than that described for polyaniline in this article.

2. Experimental details

2.1. *Preparation of polyaniline*

To a $100\,cm^3$ mixture of NH_4F, HF (Comuhrex co. 26701, Pierrelate, France), 0.05 moles ($4.6\,cm^3$) of freshly distilled aniline (Prolabo) were added with agitation. The oxidant, 0.04 moles (8.4 g) of ammonium persulphate, was dried under vacuum and added, with agitation. After a few minutes a green colour appeared and then a black precipitate. Agitation was continued for 1 h. The mixture was then diluted with a large volume of water, and the black precipitate was filtered off and washed, firstly by a Soxhlet extraction with water for 24 h, then with acetonitrile for 48 h. It was then dried under vacuum. The polyemeraldine form obtained was 'doped' by agitation in aqueous media with different acids, for 48 h at pH 0 or for one week at pH 3. The doped material was then purified further by Soxhlet reflux in acetonitrile for 12 h, to eliminate excess acid and water. It was finally dried under vacuum.

2.2. *Preparation of the battery*

2.2.1. Conditioning of the electrodes. Positive electrodes of area $1\,cm^2$ were formed from a mixture of polyaniline, 20% by weight black acetylene and a grill of stainless steel which served as collector. This mixture was compressed under a force of 3 tonnes to form a pellet. Generally the weight of the pellet was about 20 mg, but it was possible to form satisfactory pellets of 100 mg and more from polyaniline. The thickness of a pellet, consisting of 100 mg of polyaniline and 20% carbon, was slightly greater than 1 mm for a diameter of 13 mm. The collector could also be made from aluminium.

2.2.2. Drying of the electrodes. The electrodes were dried under vacuum at 80° C to eliminate any residual water from the polymer and thus yield more reproducible results.

2.2.3. The negative electrode. The negative electrode was formed by electrochemical deposition of lithium into aluminium in propylene carbonate (1 M in $LiClO_4$) and with a current density not exceeding $1\,mA\,cm^{-2}$. It must be noted that with this current density, the lithium diffuses into the aluminium resulting in an alloy of lithium/aluminium of up to 50%. However, during this electrochemical insertion reaction the potential of the electrode is always less negative than the potential of a lithium electrode, by not less than 330 mV.

2.2.4. The electrolyte. The most commonly used electrolyte is lithium perchlorate solution, which is 1 M in propylene carbonate. Lithium perchlorate (GFS Chemical Cie) was dried at 100° C under secondary vacuum for 30 h. The secondary vacuum at 100° C yields a very dry salt. The residual water concentration was verified by the Karl Fischer coulometric

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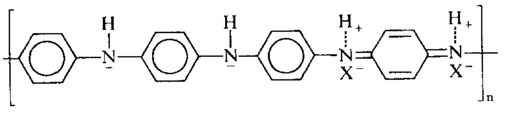
method and gave 1-2 × 10^{-6} mol g^{-1} of water. If the temperature of drying reaches 150° C or more, some degradation of the perchlorate occurs, probably yielding other chlorates. Effectively, these latter salts could react with the Karl Fischer reagents yielding water content results which are completely erroneous. The propylene carbonate (PC) (Fluka) was distilled twice over sodium in a glove box. The degree of humidity of the complete electrolyte (solvent + salt) was in the order of 10^{-4} M. This dosage was achieved using a Tacussel aquaprocessor which was installed in a Jaram glove box. The electrochemical cell and the construction of the battery have been described in a patent [11]. The volume of electrolyte used was in the region of 2 cm^3. An original assemblage for 7 batteries in parallel was made from current generators made at DEIN/LERA in the Centre d'Etudes Nucleaires de Saclay. The whole system was controlled by a Sirius microcomputer.

3. Results and discussion

From the studies carried out, it was evident that the mode of preparation of the aniline, the treatment carried out on the polymer and the system of employing the electrodes were of considerable importance to the performance of the battery. The acid media used for the preparation of the polyaniline are in particular: sulphuric acid at pH 1 [14, 18] and 2 [4, 12, 15, 16], hydrochloric acid at pH 1 [14, 18], nitric acid at pH between 0 and 1 [14, 17, 18], hydrofluoric acid at pH 2 [19, 20] and perchloric acid [2, 13, 18]. The mechanism for the formation of polyaniline essentially involves an initial step of head-to-tail dimerization of the aniline cation radical with the loss of two protons [21]. The medium used in the formation of the polyaniline must, therefore, answer a number of criteria, particularly strong acidity, a weak nucleophile and a particular ionic activity [22].

We have observed that an eutectic mixture of NH_4F, 2.3 HF gives the best results with regards to the molecular mass [23] and polymer stability, when examined voltammetrically in organic medium [13]. Other studies by RPE *in situ* [24] have shown that the polymer obtained in this organic medium by electrochemical means contains a very low number of structural defects, resulting from linkages other than the head-to-tail linkage of the aniline molecules. The polyaniline obtained by oxidation by ammonium persulphate in the NH_3-HF mixture is generally in the polyemeraldine form (I) doped with sulphuric acid. It only contains a small quantity of fluoride (probably substituted on aromatic rings) which is detectable by fluoride NMR on the polymer in the solid state [25].



(I)

X = sulfate anions.

In this structure, it is likely that only the imine nitrogens are in the protonated form and not the amine nitrogens. In effect the protonation of the former constitutes a doping reaction [26] which increases the conductivity, with a corresponding p*K* of 6, whereas the p*K* of the amine functions is approximately 2. By comparison, the complexation of sp3 nitrogens interrupts the conjugation of the polymer and here decreases its conductivity.

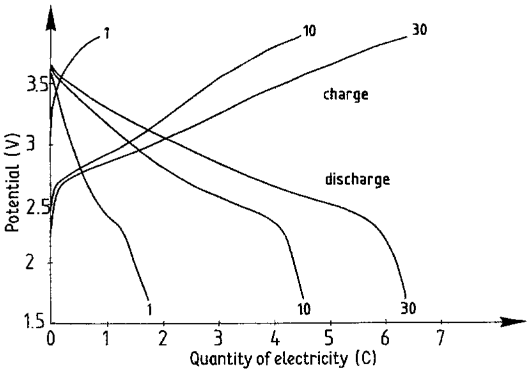
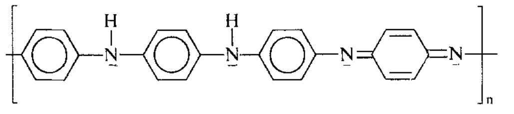


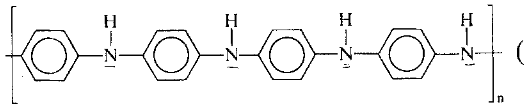
Fig. 1. Charge–discharge curves of polyaniline battery (17.5 mg) + carbon 20%/PC + $LiClO_4$/Li–Al. Polyaniline was chemically prepared in NH_4F, 2.3 HF then protonated at pH 3 for 12 h. Cycles were made at 25° C between 1.7 and 3.9 V at 0.5 mA. The capacity was stable after the 25th cycle (103 Ah kg^{-1}). 1, 10 and 30 are the 1st, 10th and 30th cycles.

If this material is well washed with water with the aid of Sohxlet extraction, the protons are totally eliminated resulting in a polyemeraldine in the basic form (II).



(II)

It has been shown that the protonated form I is conducting (approx. 10 S cm^{-1}) and that form II is non-conducting [27]. It is also possible to completely reduce the polyaniline with hydrazine to polyleucoemeraldine III:



(III)

This operation must be carried out in a glove chamber, because this reduced form of polyaniline is reversibly oxidized by atmospheric oxygen. It will be seen at a later stage that polyleucoemeraldine can equally be used as the active material in a battery.

3.1. *Polyemeraldine as battery electrode*

3.1.1. Influence of pH and type of acid used for doping the polyaniline. The extent of protonation of the polyaniline samples is very important. If it is not sufficient, the doping which occurs during cycling of the battery results from protons and anions in the solvent (these protons can result from residual water). The capacity of the polyaniline generally increases progressively in the course of cycling, reaching a maximum at the end of 30 cycles, as seen in Fig. 1. This sample of polyaniline has been protonated (doped) by allowing it to equilibrate in an aqueous solution of perchloric acid (pH = 3) for only 12 h.

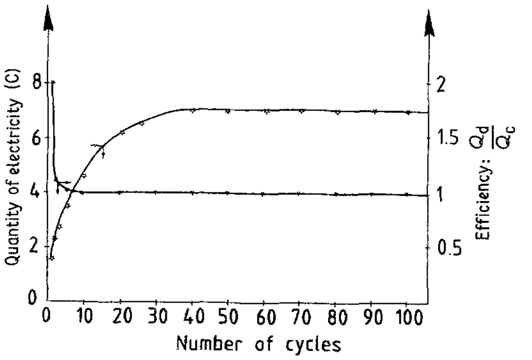


Fig. 2. Capacity and faradaic yield as function of cycle number from the experiment of Fig. 1, but with 18.5 mg of polyaniline. After the 40th cycle the capacity was constant (105 Ah kg^{-1}) for several hundred cycles.

Figure 2 resulted from a series of similar experiments, and represents the coulombic output and the discharge capacity of polyaniline as a function of the number of cycles. It has been established that during the first few cycles the number of coulombs of discharge recovered is in fact greater than the number of coulombs charged. This is explained by the fact that initially the polyaniline is already in a state of charge corresponding to the polyemeraldine state, and during the cycling of the battery the electrolyte penetrates progressively into the polymer.

Figure 1 was therefore obtained from a polyaniline sample which had been insufficiently protonated. On the other hand, for polymer in an aqueous solution of perchloric acid of pH 3, for 10 days instead of 12 h, a material was obtained which exhibited the cycling behaviour shown in Fig. 3. In effect, under the conditions of the experiment, the polymer reached its maximum capacity after only a few cycles.

The following acids were used for doping the polyaniline: perchloric, sulphuric, fluoroboric, benzenesulphonic and hydrofluoric. The investigations were carried out at different pHs in aqueous solution, and also in solutions of water and acetonitrile. It was established that the protonation reaction was faster in more concentrated solutions and that the material reaches its maximum capacity in the presence of propylene carbonate. If the pH of the aqueous solution used to equilibrate the level of protonation of the polyaniline was more than 4, a decrease in the discharge capacity (Ah kg^{-1}) of about 25% was observed. This is due to the conductor/insulator transition observed during the measurement of the conductivity of the polymer as a function of pH of the solution in which the polymer had been equilibrated [27–29]. This can equally be correlated with the pK_as of the polymer which were around 2.5 and 5.5 [30] and which correspond to two types of nitrogen atoms contained by the macromolecule, the aromatic amine functions and the imine functions.

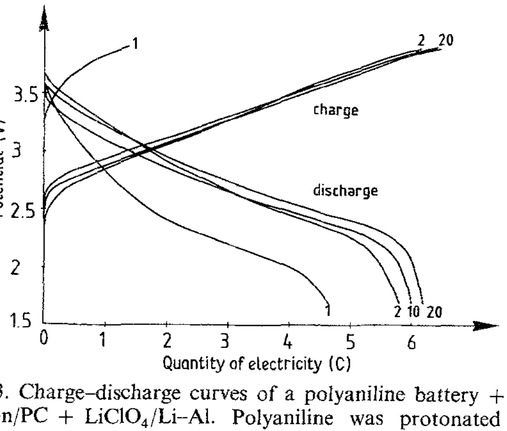


Fig. 3. Charge–discharge curves of a polyaniline battery + 20% carbon/PC + LiClO$_4$/Li–Al. Polyaniline was protonated with HClO$_4$ at pH 3 for 10 days. Conditions as in Fig. 1. 1, 2, 10 and 20 are the corresponding charge–discharge cycle numbers.

The dopant anions, such as fluorides, sulphates or bisulphates, whose lithium salts are only slightly soluble in propylene carbonate, do not seem to have a great influence on the discharge capacity of the polyaniline. It was always observed than the maximum capacity was obtained after a greater number of cycles, than when the polymer was doped, for the same pH, using either perchloric or fluoroboric acid. This observation is in fact contradictory to the results obtained by Okabayashi [31], which indicated that the discharge capacity was lower when the polymer was doped with anions whose lithium salts are insoluble. Possibly these authors did not carry out sufficient cycles to permit the full capacity of the electrode to be established.

The utilization of an insoluble anion dopant in the presence of lithium is of great interest. In effect, if it is really insoluble, it would remain fixed along the polymer chain and not diffuse into solution. In this case the positive charges on the doped polyaniline would have to be compensated for, at the first reduction, by the arrival of lithium cations. In this manner the polymer would function as a material for the insertion of lithium and the battery, which would use the lithium as a negative electrode, could be used with a thin film of electrolyte, since only the transport of lithium would assure the passage of current between the two electrodes. It is probable that in the course of the cycling, the sulphide ions, sulphates or bisulphates, gather in clusters or crystals and so do not play any part in the process of compensation of charge in the heart of the polymer. This interpretation is drawn from NMR results, which show that the signal of the lithium present at this time is very much characteristic of the signal of 'solid' lithium [25].

3.1.2. Influence of the nature of the oxidant. Polyanilines can be obtained by oxidation of aniline using various oxidants [27, 32, 33]. In general, it suffices to utilize a reagent with a potential slightly greater than 0.8 V (ENH). Studies carried out by Yu *et al.* [34] have since led to the use of ammonium persulphate as the most popular oxidant. For industrial application of polyaniline, it would be interesting to find a less expensive oxidant than persulphate (which is generally prepared by electrolysis) and one which gave higher capacity. NH_4F, 2.3 HF mixture was unquestionably the best medium, and gave the best yields for synthesis of polyaniline. Furthermore a very stable material was obtained as rechargeable electrode in a secondary battery. The choice of oxidant is very limited: effectively, it must be soluble in the NH_4F, 2.3 HF mixture.

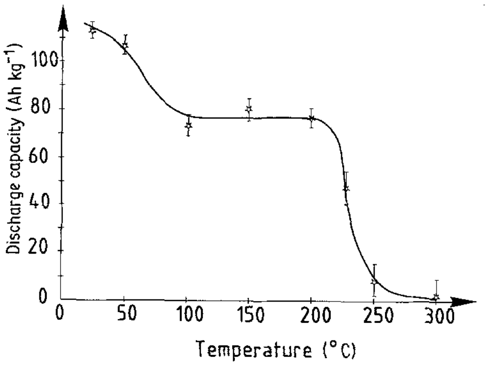


Fig. 4. Discharge capacity of polyaniline in a pellet with 20% carbon as a function of drying temperature under primary vacuum for 4 h. Temperature from 25 to 300° C.

Tests have also been carried out using, for example, salts of permanganate, dichromate, iodate, persulphate and oxygenated water. The results show that the use of ammonium persulphate gives a yield that is practically quantitative (99%) (compared with, e.g. dichromate which gives a yield of 84%) and, furthermore, results in a material which has the best discharge capacity (20% more by comparison with the polymer prepared using dichromate) and excellent stability as a battery electrode. It was noted that the persulphate was the only oxidant used that did not result in the liberation of water during the course of the reaction. In consequence it proceeds in a relatively anhydrous condition.

Taking into account the polymerization reaction and the doping of the polymer at 0.7 electrons per cycle [7, 13], the stoichiometry of the reaction is as follows:

$$nC_6H_5NH_2 + 1.35nS_2O_8^{2-} \longrightarrow ((C_6H_4NH)^{0.7+})_n, \quad n0.35SO_4^{2-} + nSO_4^{2-} + 2nH^+$$

It has not been possible to clarify the connection between the redox potentials of the oxidants used and the yields or properties of the polyanilines obtained.

Apparently, there is no correlation between the conductivity of the polyanilines in the solid state and the discharge capacity or its stability in the secondary battery.

The electrical conductivity of the polyaniline is a function of the acid used for doping [19], the level of protonation [27] and the extent of water of solvation [35]. The discharge capacity and the stability of the polymer are equally functions of the same parameters, but they are also more sensitive to structural defects and the molecular mass of the material. It appears that the influence of defects in the structure on the conductivity are less important in the case of polyaniline than in the case of polyacetylene [36].

3.1.3. Thermal stability. Figure 4 represents the results of a series of tests concerning the discharge capacity of the polyaniline electrodes obtained during cycling at 0.5 mA cm^{-2}, as a function of the temperature at which the electrodes were dried under vacuum. There are three distinct zones. The first zone from 40 to 80° C corresponds to the elimination of water of solvation of the ions contained in the polymer. Between 80 and 200° C is the zone of stability of the material and above 200° C is a zone marking the decomposition of the polyaniline.

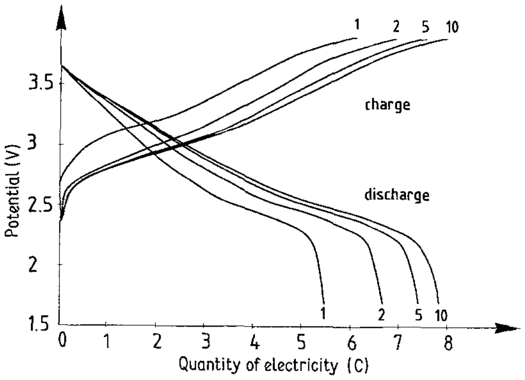


Fig. 5. Charge–discharge curves of polyaniline battery (19.4 mg + 20% carbon). Polyaniline was reduced by hydrazine. Conditions are the same as in Fig. 1. After the 10th cycle, the capacity is constant (113 Ah kg^{-1}).

Although a better discharge capacity is obtained for polyaniline dried at room temperature, it was found that drying at 60° C for 2 h yielded discharge capacity values that were perfectly reproducible.

3.2. *Polyleucoemeraldine as an electrode for a secondary battery*

The totally reduced form of polyaniline can be obtained by chemical reduction of polyaniline with hydrazine in the absence of oxygen. This form, although being initially an insulator (8 × 10^{-8} S cm^{-1}) [30], can be used without protonation as electrode material in association with black acetylene.

The curves in Fig. 5 were obtained by cycling between 1.7 and 3.9 V at 25° C. In comparison to Fig. 1, it can be seen that a greater charge is necessary for the first charge cycle. But the nominal capacity of the battery is (113 Ah kg^{-1}) obtained at the end of only a few cycles.

It is possible to employ current densities as high as 5 mA cm^{-2} and still retain 40% of the value obtained at 5 mA. On the other hand we have observed a decrease in the stability of this material compared to protonated polyemeraldine. In effect, after 60 cycles the capacity begins to diminish, due to degradation of the negative electrode. In other respects, the use of this polymer in its reduced form is very difficult because it requires the permanent use of an inert atmosphere.

3.3. *Behaviour of the battery*

In order to consider this type of battery based on polyaniline on a commercial basis, it would be necessary to perfect the manufacture of all the constituents.

The preparation of the Li–Al electrode posed no major problems, taking into consideration the importance of the thickness of aluminium and allowing that the quantity of lithium deposited is at least two times greater than the amount necessary for cycling of the polymer. The negative electrode was held firmly by the casement of the cell during the deposition of lithium, thus avoiding unwanted deformation as observed with a self-supported aluminium electrode. As far as the electrolyte is concerned, the concentration of salt in solution employed in the investigation was higher than that required for the number of coulombs used. However, we have been able to perform several experiments with lower salt concentration than is necessary, because of a contribution of lithium cations in the current transport.

The solvent which gives the best results, as regards polyaniline, was found to be propylene carbonate. Certain ethers, which are described as being relatively stable with lithium [37], appear to degrade. Effectively, the solvent must resist not only the lithium/aluminium alloy, but also the potential of the polyaniline (3.6 V) and the voltage during charging, which can reach 3.9–4 V and oxidize the ether.

The charge and discharge reactions of the battery are a combination of the following reactions:

$$\mathrm{PANi} + \mathrm{Al} + \mathrm{Li}^+ + \mathrm{ClO}_4^- \rightleftharpoons \mathrm{PANi}^+, \mathrm{ClO}_4^- + \mathrm{Li{-}Al}$$

$$\mathrm{PANi}, \mathrm{ClO}_4^-, \mathrm{Li}^+ + \mathrm{Al} \rightleftharpoons \mathrm{PANi}^+, \mathrm{ClO}_4^- + \mathrm{Li{-}Al}$$

In effect, in organic medium and in the presence of perchlorates, the polyaniline functions partially by insertion of lithium. Sariciftci *et al.* [38] have shown, by *in situ* Raman spectroscopy, that the perchlorate anions remain trapped in the polymer during the cycles restricted to the first electron transfer of the polymer [24]. On the other hand, as soon as the cycling reaches the potential corresponding to the second transfer, the perchlorates enter and leave the polymer as it is oxidized, then reduced. It should be noted that the first transfer is responsible for at least 60% of the capacity of the polyaniline [7].

In reality, if one chooses to work in a restricted electrolyte, a certain number of new difficulties arise. The most important is, probably, the fact that the polymer dries out in the solvent, giving rise to volume variations during the charge and discharge cycles.

3.3.1. Influence of temperature. Cycling tests carried out at temperatures from +60 to 0° C show that the usable discharge capacity decreases by only 30%. At 60° C with 0.5 mA cm^{-2} the capacity is near 150 Ah kg^{-1}. Variations in the capacity of polyaniline with temperature have been attributed to the increase in the ionic conductivity of lithium carbonate, 1 M in lithium perchlorate, and to the diffusion coefficient of the ions in the polymer. Since polyaniline performs better at elevated temperatures, it is possible that a battery based on this material could find numerous applications.

3.3.2. Influence of current density. The usable capacity, therefore, is obviously a function of the current density. In a cell which has the positive and negative electrodes 1 cm apart, with an electrode containing 20 mg of polyaniline and at room temperature, the capacity decreases by a factor of 2.7 as soon as the current density of the discharge changes from 0.5 to 5 mA cm^{-2}, the charging current density being maintained at 0.5 mA cm^{-2}.

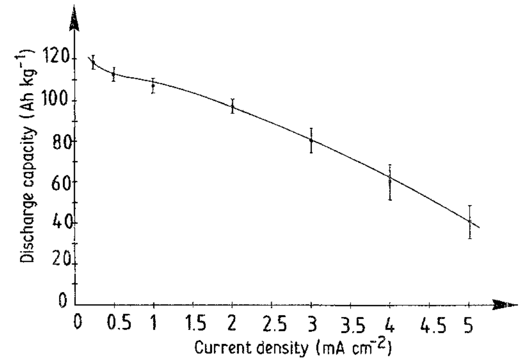


Fig. 6. Discharge capacity of polyaniline in a battery as a function of the discharge current. Polyaniline was reduced by hydrazine. Charge current was constant at 0.5 mA. Other conditions are the same as in Fig. 1.

Figure 6 shows results obtained with a battery containing polyaniline which has been reduced by hydrazine (polyleucoemeraldine). Very similar results are obtained with polyemeraldine. It was noted that with discharges of 5 mA cm^{-2} it was not possible to carry out a large number of cycles. Furthermore, with such a current density a rapid degradation of the polyaniline pellet is observed, probably because the mixture of polyaniline and the carbon cannot mechanically withstand the rapid variations in the volume of the polymer provoked by the movement of ions within it. Such current densities can, therefore, only be used with these pellets for relatively short times.

The decrease in capacity when current density was increased is a consequence of the large internal resistance of the battery, of diffusion coefficient values (about 10^{-10} cm^2 s^{-1} [7]) of the ions for penetration of the polyaniline/carbon composite and of the polyaniline chains themselves.

3.3.3. Self discharge and behaviour in permanent charge (floating). These two characteristics are better for batteries based on aniline than for the majority of other types of battery in existence. In effect, the self discharge is very slow. Thus, after three months storage the discharge capacity diminishes by only 8%. After recharge, the nominal capacity can be recovered. The only important change observed in the charge/discharge curves after storage was an improvement in the discharge plateau slope.

The stability under permanent charge is equally good. A permanent voltage of 3.6 V can be applied. Indeed, when the battery is charged, the current passing is practically zero. After 75 days of charging at this level, the capacity at the first discharge with 0.5 mA increases by around 10%.

4. Conclusion

Polyaniline used as the active electrode material in a secondary battery exhibits a greater discharge capacity than any other conducting polymer studied so far. Its maximum capacity is approximately 150 Ah kg^{-1}. This capacity is obtained after a very slow charge and discharge at a temperature in the region of 60° C. At room temperature (25° C) under a current of 0.5 mA cm^{-2} and the concentration of water at a minimum, the capacity of the polymer is 100 Ah kg^{-1} and is very reproducible for many hundreds of cycles. The usable capacity is, therefore, a function of the ambient temperature and also of the degree of residual humidity of the polymer and the conducting properties of the electrolyte. The current densities employed at room temperature for materials in the range 10–15 mAh cm^{-2} must not exceed 5 mA cm^{-2} in an intermittent flow, when using propylene carbonate as the solvent. Naturally, with thinner layers it is possible to obtain higher currents, but nevertheless these cannot exceed 10 mA cm^{-2}. The polyaniline electrode is effectively very stable. If a decrease in the capacity is observed during the life of the battery, it generally suffices to change the electrolyte and the negative electrode to regain the nominal capacity of the battery.

Polyaniline prepared in a NH_4F, 2.3 HF mixture yields a material of high molecular weight which is very stable for use in a secondary battery. The feasibility of a polyaniline/propylene carbonate-$LiClO_4$/Li–Al battery has been demonstrated. Such a battery is characterized by a very slow self discharge, a good stability on constant voltage (floating) and a faradaic efficiency of 100%. The voltage on open circuit at full charge is 3.6 V. The usable voltage is, on average, from 2.8 to 3 V. The maximum disposable energy density is therefore in the order of 300 Wh kg^{-1} not including the solvent, the negative and the packing. With this in mind, and with appropriate technology, it is possible to imagine a battery having an energy density in the region of 100 Wh kg^{-1}. The limiting factors lie with the conducting properties of the electrolyte and the stability of the negative electrode. Mixtures of propylene and ethylene carbonate show a slight improvement for current densities between 0.1 and 2 mA cm^{-2}.

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