CONTRACT SPC-93-4033

4th two-month Progress Report

February-March 1994

Introduction

In this 4th two-month period we have continued the investigation of the performance and characteristics of new thin-layer Li- M_XWO_4 (M=Ag, Cu) batteries. Preliminary results concerning these batteries were described in the 1st two month report. The aim of the work is that of exploring the potentialities of the highly conducting gel electrolytes for the development of lithium polymer batteries having properties of interest for the electronics market and, in particular for military uses. This work completes task (ii) as planned in the project program (see 1st two month report).

Task (ii) - Applications of PAN-based gel electrolytes. Lithium polymer batteries.

Introduction.

The type and the unique structure of the batteries developed within this Project have been already described in the 1st two month progress report. Basically, the novelty of these batteries is that they use new-concept, low-resistance cathode materials in connection with the highly conductive, PAN-based gel electrolytes. This combination gives very flat (constant voltage) discharge curves and high-performance operation at ambient and subambient temperatures.

Experimental.

The batteries are fabricated in a laminated structure which includes the sequence of a lithium metal anode strip, a polymer electrolyte film and a composite cathodic membrane (see 1st two-month progress report). We have use two types of cathodic membranes differing from the nature of the active electrode material which was in one case Ag_2WO_4 and in the other $CuWO_4$.

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Silver tungstate, Ag_2WO_4 was prepared by adding an aqueous solution of silver nitrate to an aqueous solution of sodium tungstate (2). The precipitate was washed and dried at 60°C under a nitrogen stream. The purity of the final Ag_2WO_4 salt was controlled by x-ray powder analysis. Copper tungstate, $CuWO_4$ was prepared by heating at 850°C for 15 hours an intimate mixture of copper oxide and tungsten oxide. Also in this case the purity of the so obtained $CuWO_4$ salt was controlled by x-ray powder analysis

The cathodic membranes are formed by blending a mixture of carbon black and the electrochemically active compound (Ag_2WO_4 or $CuWO_4$) with poly(vinyl chloride) PVC. The active compound provides the battery capacity, while the carbon and the polymer additives confer the electronic conductivity and the plasticity, respectively, to the whole cathodic membrane. We have used the following cathode compostion (in weight ratio): M_xWO_4 =: 75%, C=5% and PVC=20%

Results

1. Lithium-silver tungstate polymer battery

The battery studied has the structure:

$$Li\ /PAN,LiClO_4\ PC,EC\ /\ Ag_2WO_4\ ,\ C,\ PVC \qquad [1]$$

and an open circuit voltage (OCV) of 3.4 V at room temperature which is related to the following main discharge process:

$$2Li + Ag_2WO_4 \ ==>\ Li_2WO_4 + 2Ag \qquad [2]$$

As already pointed out in the previous report, the battery has the unique, important feature of using a highly conducting with a polymer electrolyte and of being based on a displacement discharge process which produces the Li_2WO_4 compound and the Ag metal (see [2]). Since this process is based on a multi-phase reaction, the discharge voltage remains fixed until completion of the electrochemical balance, namely, until the consumption of two faradays per Ag_2WO_4 mole. The constancy of the discharge voltage is also assured by the progressive production of finely dispersed silver which provides contact throughout the entire cathodic mass and this consistently contributes to minimize ohmic polarizations during discharge.

This is clearly shown by Figure 1 which illustrate typical discharge curve run at a various discharge rates. The exceptional flatness of the curve, which remains constant around 3.3 V for the entire discharge, is evident.

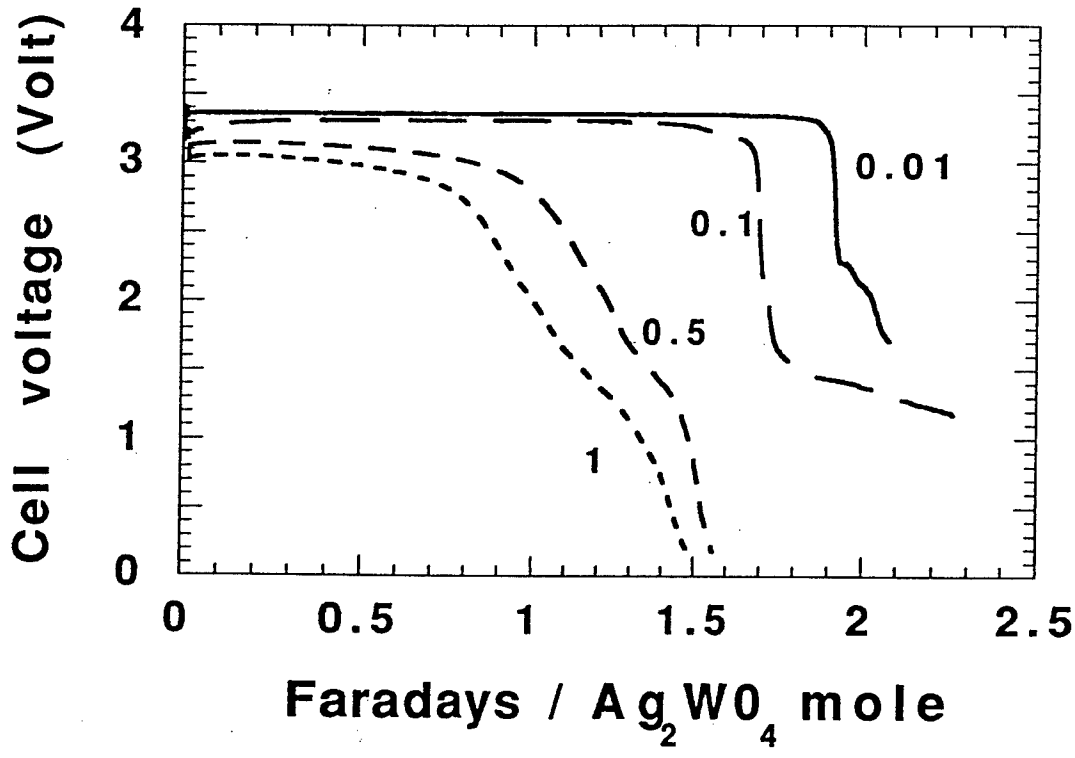

Figure 1- Discharge curves of the Li/Ag_2WO_4 thin-film, polymer battery at room temperature and at various rates. The values of discharge current densities are given in $mAcm^{-2}$.

Other interesting features of the Li/Ag_2WO_4 battery (already discussed in the previous report) are the occurence of a second discharge plateau (which can be profitably used to buffer otherwise catastrophic effects, such as those associated to incidental overdischarge and shortcircuiting) and the continuous dispersion during discharge of silver in the cathodic mass (see [2]) an event which favours high rate capabilities.

It is also important to report that, although the Li/Ag_2WO_4 battery performs preferably in the primary mode, there are indications that also a partial, but yet efficient, rechargeability can be achieved. In fact the battery is capable to sustain several shallow (i.e. limited to 20% of the theoretical capacity) charge - discharge cycles, with the typical trend illustrated in Figure 2. By adding the capacity delivered at each discharge cycle one

obtains a total value which largely exceeds the theoretical capacity (see Figure 3), and this demonstrates the effective rechargeability of the battery. However, and as already pointed out, this rechargeability is limited to the first plateau only and it appears to be efficient only under shallow regimes. On the other hand, even if partial, the recheargeability may be considered another useful bonus of the Li/Ag_2WO_4 battery.

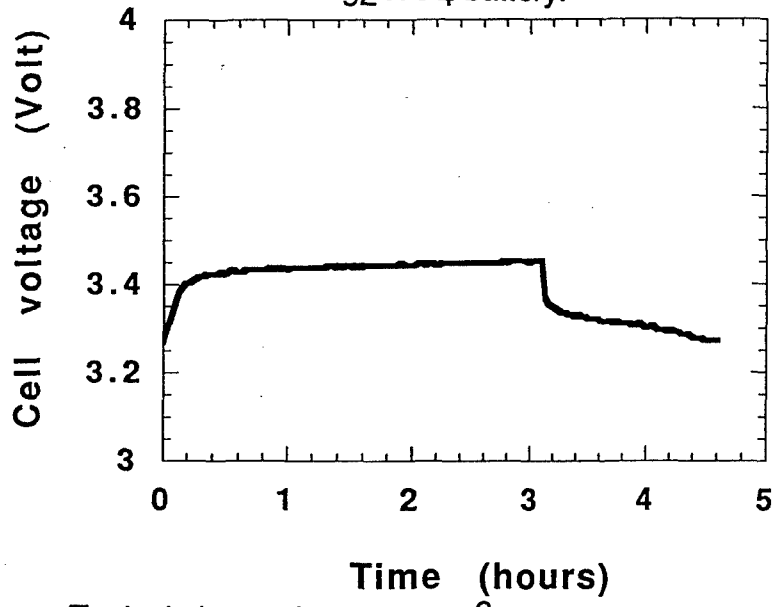

Figure 2- Typical charge (0.05 $mAcm^{-2}$ rate) - discharge (0.01 $mAcm^{-2}$ rate) cycle of the Li/Ag_2WO_4 thin-film, polymer battery at room temperature.

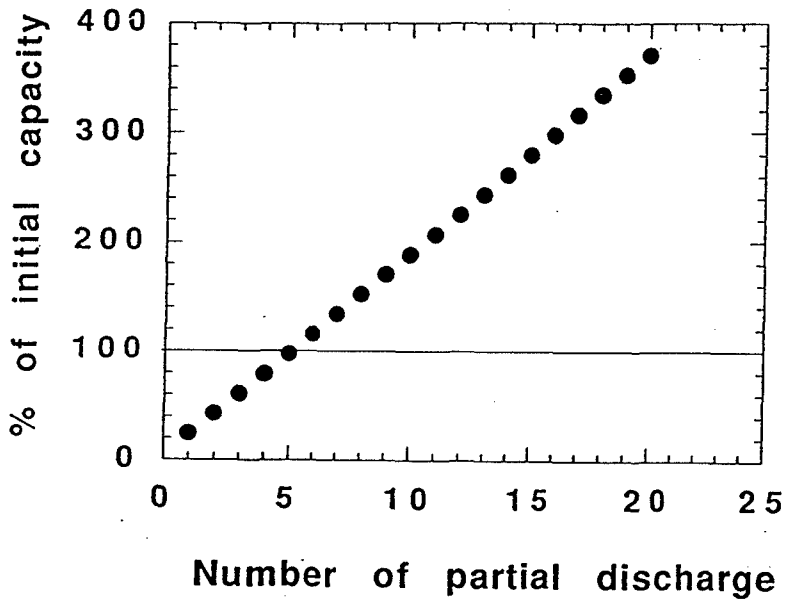

Figure 3- Percent of the theoretical capacity calculated as the sum of each discharge capacity produced during 20 cycles of the Li/Ag_2WO_4 thin-film, polymer battery. Room temperature.

All these favourable aspects may be contrasted by a relatively low energy density (188 $Whkg^{-1}$ theoretical) and by the high cost of the silver cathode. However, these drawbacks are expected to be counterbalanced by the unique performance of the battery. Beside, we expect that other metal oxide cathodes having comparable behavior and improved weight and cost characteristics, can also be considered. One possible example is copper tungstate.

2. Lithium-copper tungstate polymer battery

The battery :

$$Li\ /PAN,LiClO_4\ EC,PC\ /\ CuWO_4\ ,\ C,\ PVC \qquad [3]$$

has an open circuit voltage (OCV) of 2.8 V at room temperature which is related to the following main discharge process:

$$2Li + CuWO_4 \Longrightarrow Li_2WO_4 + Cu \qquad [4]$$

This battery has characteristics similar to those of the Li/Ag_2WO_4 battery. First, it uses the same highly conducting polymer electrolyte and, as the latter, its main discharge process is a displacement reaction which produces the Li_2WO_4 compound and the finely dispersed Cu metal. Therefore, also for the $Li/CuWO_4$ battery a flat discharge plateau and an effective control of the ohmic polarization are expected. This is confirmed by Figure 4 which reports the discharge curves at various rates and by Figure 5 which shows the voltage response and the voltage recovery of the battery following discharge pulses. Also in the case of the $Li/CuWO_4$ battery a good fraction of the theoretical capacity is delivered at high rates and the voltage recovery after pulse discharge is very fast.

One feature of the silver-based battery which is not matched by the copper-based analogue, is the partial rechargeability. In fact, attempts of cycling the $Li/CuWO_4$ battery were unsuccessful. The reason for this unexpected difference between the two batteries is presently not clear.

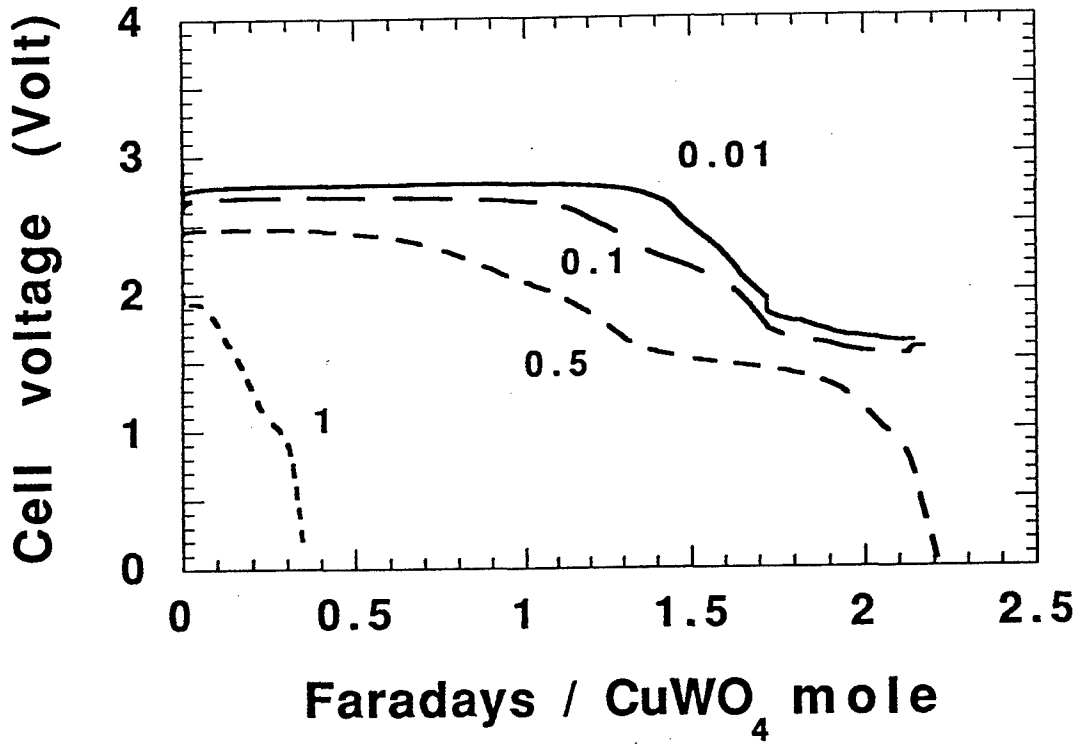

Figure 4- Typical discharge curves of the Li/$CuWO_4$ thin-film, polymer battery at room temperature and at various rates. The values of discharge current densities are given in $mAcm^{-2}$.

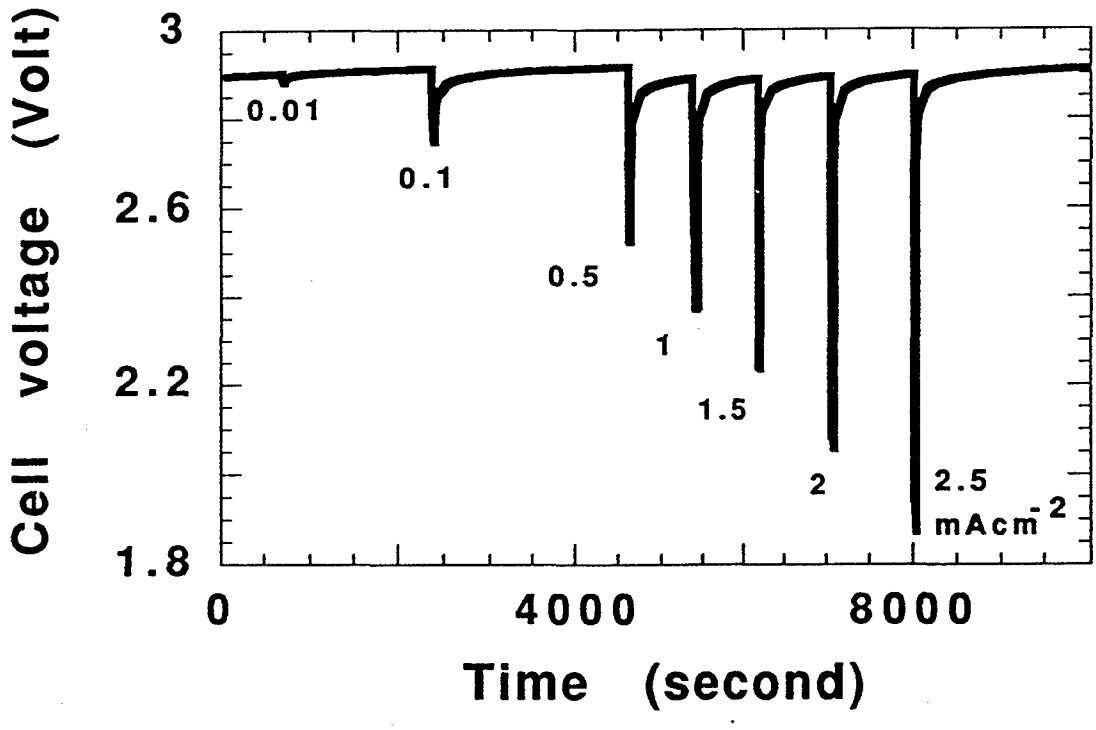

Figure 5- Voltage response and voltage recovery of the Li/$CuWO_4$ thin-film, polymer battery at room temperature following various-rate galvanostatic pulse (30 s) discharges.

Conclusions

The above reported results suggest that the Li/CuWO4 and, especially, the $LiAg_2WO_4$ battery are worth of attention for a series of reasons. They are in essence:

i) The nature of the electrodic reaction, which is different from the common intercalation processes, has the unique advantage of providing a flat, high- value voltage discharge plateau and high-rate outputs.

ii) The discharge process develops in two steps, the main one around 3V involving 2 faradays per cathode mole and a second one around 1.5V involving an extra 0.5 faradays per mole. The occurrence of the second discharge step gives availability of extra capacity which can be used to buffer catastrophic effects which may be incidentally induced by overdischarge and/or by short circuiting. Reliability is also assured by the wide stability window of the electrolyte.

iii) Although the battery performs preferably in the primary mode, there are indications that also shallow cycling can be achieved at least for the Li/Ag_2WO_4 battery.

iv) The novelty of Li/Ag_2WO_4 and $LiCuWO_4$ electrode combinations which, although exploited some years ago in our laboratory in liquid systems , to our knowledge have never been used before for lithium solid-state, polymer batteries.

v) The suitability of these batteries as ideal power sources for the consumer electronics and for military uses.

vi) The possible drawback of the $LiAg_2WO_4$ battery, namely its relatively low energy density combined with a high cost, is expected to be counterbalanced by the unique performance of the battery itself. Furthermore, other metal oxide cathodes, having comparable behaviour and improved weight and cost characteristics, of which copper tungstate is a possible example, can be used in alternative.