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Design concepts of high power bipolar rechargeable lithium battery

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Abstract

The present study shows that current bipolar Li/TiS_2 batteries using a 0.38 mm thick TiS_2 bipolar plate, can yield moderate specific power and also high specific energy battery. The computer design studies project that a 100 V, 10 A h bipolar Li/TiS_2 battery can achieve 150 W h/kg, 210 W h/l, and 150 W/kg. The unoptimized experimental bipolar Li/TiS_2 batteries (3 cells, 90 mA h) exhibited 47 W h/kg, 90 W h/l, and 140 W/kg. Preliminary results on the cycleability of the bipolar batteries were demonstrated. The results also show that enhanced rate capability can be achieved by using pulse discharge and longer rest period between pulses.

Introduction

Recently, there has been an increase in demand for high power, high specific energy sources for several applications including electric vehicles [1]. Conventionally, batteries are low power and high capacity energy sources. In order to improve power performance, an improved battery design is required. The bipolar design is known to provide higher power output over the existing monopolar design. High pulse power lead/acid bipolar batteries are under development to meet Air Force requirements [2]. However, the specific energy of lead/acid batteries cannot satisfy many applications which require high specific energy as well as high power. A rechargeable battery that provides both high specific energy and high specific power would be an attractive power source candidate for many applications.

Lithium batteries are known for their high specific energy. Small capacity rechargeable Li cells of monopolar design such as Li/TiS_2, Li/CoO_2, Li/MoS_2, Li/$NbSe_3$, Li/SO_2, Li/$CuCl_2$, Li/V_2O_5, Li/MnO_2, and LiC/CoO_2 are currently being developed (Table 1). These batteries have high specific energy, e.g., the Li/TiS_2 battery has 125 W h/kg, compared with other rechargeable battery systems (30–50 W h/kg). Combining the Li battery with a bipolar design may result in a useful power source for many applications. Titanium disulfide has been demonstrated to be a highly reversible material in secondary Li batteries [3]. Koch [4] has reported that thin, oriented TiS_2 microcrystallite films were capable of delivering high current pulses. In this paper, an attempt is made to study the design concepts for bipolar rechargeable Li batteries. The Li/TiS_2 system was selected because of its long cycle life (1000 cycles at 50% depth-of-discharge) and proven performance [5].

The present study uses an empirical computer design program to examine the design options of bipolar Li/TiS_2 batteries for the high power applications. Predicted

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TABLE 1

Performance summary of small capacity rechargeable lithium cells

Cell system	Cell size	Capacity (A h) (V)	Mid-discharge voltage	Specific energy (W h/kg)	Energy density (W h/l)
Li/TiS_2	AA	1.0	2.1	120	276
Li/MoS_2	AA	0.6	1.7	55	140
$Li/NbSe_3$	AA	1.1	1.9	100	270
Li/MnO_2	AA	0.6	3.0	100	225
Li/V_2O_5	C	1.4	3.2	100	175
Li/CoO_2	D	2.8	4.0	100	207
Li/SO_2	AA	0.5	3.0	75	200
$Li/CuCl_2$	AA	0.5	3.2	75	220
Li_xC/CoO_2	A	0.6	3.6	83	204

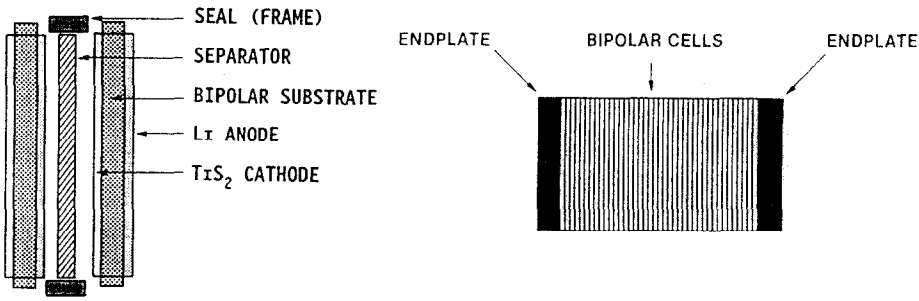


Fig. 1. Schematic diagram of a bipolar Li/TiS_2 battery.

performance outputs for various designs at various discharge rates, capacities, and voltages are reported. Experimental bipolar Li/TiS_2 batteries were fabricated and the preliminary results of the bipolar batteries are presented.

Design program

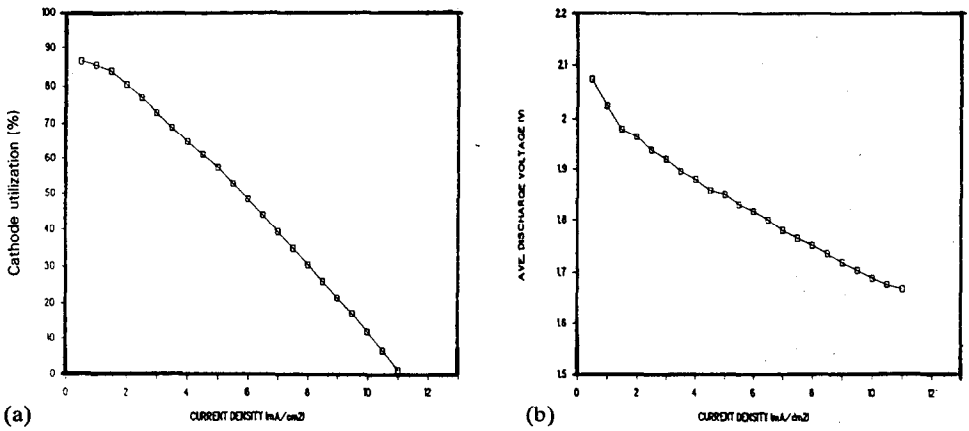
A computer design program package for bipolar batteries was developed to evaluate the effects of various design options on the performance of bipolar Li/TiS_2 batteries. A schematic diagram of a bipolar Li/TiS_2 battery is shown in Fig. 1. The computer program package includes an empirical design and data analysis programs. The program will generate a battery design based on the desired inputs and built-in component data base. This design program can be also applied to other battery systems by replacing its component design data base. The data analysis program can be used to sort the design outputs for each design input or parameter.

The major steps in the execution of the battery design computer program are: (i) determination of the actual cathode and anode capacity based on the component performance data base; (ii) optimization of bipolar plate dimension; (iii) determination of number of cells required based on battery voltage and discharge rate; (iv) calculation

TABLE 2

Important design parameters of bipolar Li/TiS_2 battery

Components	Design parameters
Cathode	Thickness, porosity, material utilization, width, height to width ratio
Anode	Anode to cathode capacity ratio, lithium foil thickness, utilization
Electrolyte	Composition, density, quantity
Separator	Type, thickness, porosity, density, no. of layers
Current collector	Density, thickness, conductivity
Frame	Material, dimension, density
End plate	Area, thickness, density
Case	Wall thickness, density, seal, overhead space



(a) (b)

Fig. 2. (a) Cathode utilization and (b) average discharge voltage at different current densities of 0.38 mm TiS_2 cathode.

of quantity of electrolyte required, and (v) design definition of other components. The design outputs are sorted by the data analysis program based on the battery capacity, battery voltage, discharge rate, etc. The effects of various design parameters/inputs on battery performance can then be analyzed.

The design inputs for the program are: battery capacity, battery voltage and discharge rate. The component design data base consists of design parameters (variables and constants) and component performance characteristics based on experimental results. Some of the important design parameters considered are: electrode characteristics (dimensions and utilization), current densities, separator dimensions, electrolyte and separator properties, and material properties of the battery hardware. Table 2 summarizes the important design parameters that have been considered in the present study. Electrode dimensions and current densities are the main variables in the program along with the design inputs. Design parameters such as: anode to cathode capacity ratio, electrode height to width ratio, thickness of the bipolar substrate, can wall thickness, number of separator layers, thickness of end plate, and the overrating factor were kept constant in this study. If required, other values for these design constants can be specified by the user.

Cathode utilization and average discharge voltage at different current densities (Fig. 2) are established from in-house experimental results of spirally-wound 1 A h cells which use 0.38 mm thick TiS_2 cathodes at 25 °C. The program details are summarized in Table 3. Issues that have not been considered to date in the study are: thermal design parameters, temperature effect on cathode utilization and the degradation of the electrolyte.

Experimental

Three experimental 3-cell bipolar Li/TiS_2 batteries were fabricated and tested at various conditions. The theoretical capacity and open-circuit voltage of the batteries are 90 mA h and 7.2 V, respectively. The batteries were cathode limited by design and their anode-to-cathode capacity ratio was 5:1. Each cell contained 0.5 ml of 1.5 M $LiAsF_6$/10% ethylene carbonate(EC) + 90% 2-methyltetrahydrofuran(2-MeTHF) electrolyte. Each battery has two bipolar plates and each bipolar plate consists of a TiS_2 cathode on one side and a Li anode on the other side. The bipolar substrate (current collector (c.c.)) is a 0.025 mm thick stainless-steel foil. TiS_2 material was procured from Degussa Co. Ethylene/propylene/diene therpolymer (EPDM) was used as the binder material in fabricating the TiS_2 cathodes. One layer of porous polypropylene separator (Celgard 2400) was used in each cell. The battery weight, without two end plates, is approximately 10 g. The bipolar batteries were sealed by compressing a polyethylene frame between two aluminum lead plates. The batteries were fabricated in dry room with a relative humidity $<2\%$.

Various tests were carried out on the bipolar batteries. Cycle-life testing was performed using a constant current charge/discharge regime. The current densities were 2.0 and 0.5 mA/cm^2 for discharge and charge, respectively. Three current densities (5, 10, and 15 mA/cm^2) were used to test the battery rate performance at both continuous and pulse discharge modes. For the pulse tests, three different pulse durations (1, 5, and 10 s) were used and with an equal rest time. For the 5 s pulse at 10 mA/cm^2, three rest periods of 5, 15, and 25 s were examined. Constant current, 0.5 mA/cm^2, were used for charge. Discharge and charge cutoff voltage limits were 4.8 and 8.1 V, respectively. All the tests were performed at ambient temperature.

Results and discussion

Computer design studies

The influence of battery capacity, battery voltage and discharge rate on specific energy (W h/kg) was studied using the design program. The effect of battery capacity (1 to 250 A h) on the specific energy of a 50 V battery as a function of battery capacity at various discharge rates (*C*/20 to 2 C) was studied. The results show that the battery specific energy increases marginally (20–30%) as the capacity increases up to 10 A h and levels off thereafter (Fig. 3). As the battery capacity increases up to 10 A h, the percentage of the nonactive material weight contribution with battery weight is reduced and thereby results in improved specific energy. The specific energy did not increase significantly beyond 10 A h due to the battery configuration that became plate-like shaped, which offsett the gain from the reduced weight of the inactive components.

The effect of battery voltage (5 to 250 V) on the specific energy of a 10 A h battery was examined at various discharge rates (*C*/20 to 2 C). The results show that

TABLE 3

Overview of computer program for bipolar battery design

Inputs	Design constants	Database	Outputs
Design capacity	Anode to cathode capacity ratio: 3 to 1	Cathode utilization versus current density	Specific energy
Battery voltage	Height to width ratio: 1 to 1	Average discharge voltage versus current density	Energy density
Discharge rate	Cathode thickness: 0.38 mm Current collector: stainless steel 0.025 mm Can: stainless steel 0.51 mm wall thickness Separator: Celgard 2400, 2 layers End plate: stainless steel 1.27 mm Over rating factor: 1.2 Electrolyte: 1.5 M $LiAsF_6$/10% EC+90% 2-MeTHF		Specific power Battery design Components dimension Component wt.%

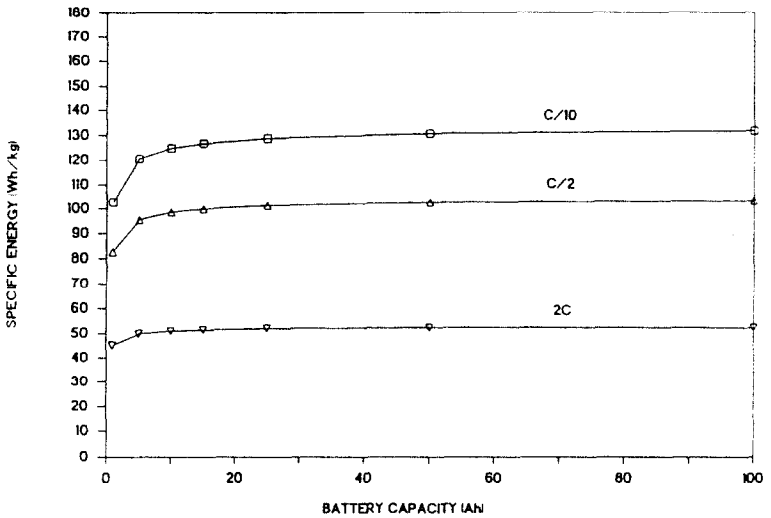


Fig. 3. The effect of battery capacity (1 to 100 A h) on the specific energy of 50 V batteries.

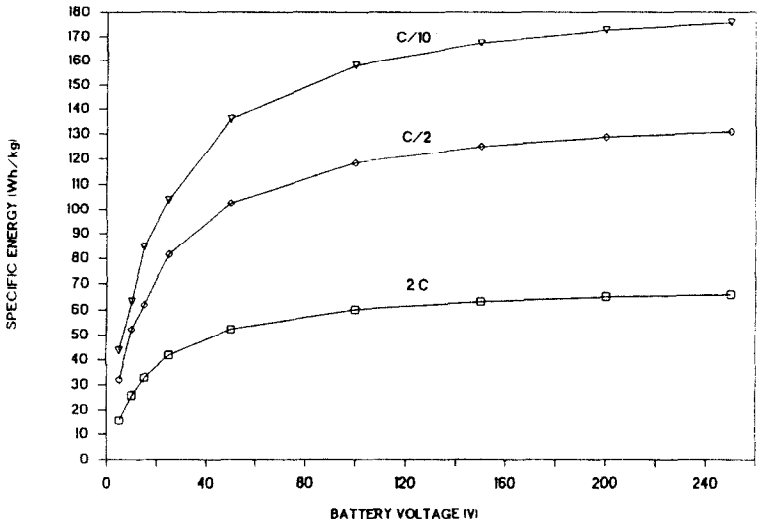


Fig. 4. The effect of battery voltage (5 to 250 V) on the specific energy of 10 A h batteries.

the specific energy is very sensitive to the bipolar battery voltage (Fig. 4). The specific energy of the batteries increases significantly for systems with voltage up to 100 V and slowly with voltage beyond 100 V. Higher voltage batteries can be cubic in shape compared with lower voltage batteries which are plate-like configuration and hence require less battery casing per unit W h. Bipolar configuration does not appear to be attractive for batteries with voltages less than 10 V.

The effect of battery discharge rate on the specific energy of 10 A h batteries was studied at various voltages (50 to 250 V) was studied. Battery discharge rates, *C*/20 to 2 C, were used. The specific energy is found to be sensitive to the discharge

rate of the battery (Fig. 5). The higher the discharge rate the lower the specific energy of a battery. A specific energy greater than 150 W h/kg can be achieved at low discharge rates. The decrease of the specific energy of the batteries is due to electrolyte conductivity and Li diffusion in TiS_2 at high discharge rates. Use of high conductivity electrolytes and thin cathode with small TiS_2 particles may improve the rate capability of the bipolar Li/TiS_2 battery.

The outputs of the program contain battery design features and projected performance characteristics (specific energy, energy density, specific power and power density). The weight budget of various components of a 10 A h, 50 V and a 50 A h, 250 V batteries are given in Fig. 6. It can be observed that 50% of the weight of the 10 A h, 50 V medium rate (*C*/2) battery is contributed by the nonactive components, such as: current collector, end plate, can, separator, and seal. However, the contribution from the nonactive components decreased to ~30% in a 50 A h, 250 V medium rate (*C*/2) battery and for this reason the specific energy of this higher capacity battery is greater by ~30% compared with the 10 A h, 50 V medium rate (*C*/2) battery. Ragone plots of these two batteries are given in Fig. 7. The maximum specific power that can be obtained from 10 A h, 50 V and 50 A h, 250 V batteries are ~130 and ~170 W/kg, respectively. The specific energy of the batteries is found to decrease with increasing specific power.

Comparison of monopolar and bipolar Li/TiS_2 batteries

Table 4 shows the performance comparison between a monopolar and a bipolar 10 A h, 50 V, medium rate (*C*/2) Li/TiS_2 batteries. The computer program used for the monopolar battery design was reported earlier [6]. The same database was used for both the monopolar and bipolar design programs. The results show that the bipolar batteries have ~40% higher specific energy and power than the monopolar batteries. These improvements are mainly due to the weight saving of the can material. The minor improvement (~15%) in energy and power densities was associated with the volume saving in the bipolar design. Improvements will be even more significant with the bipolar design at high voltage and large batteries.

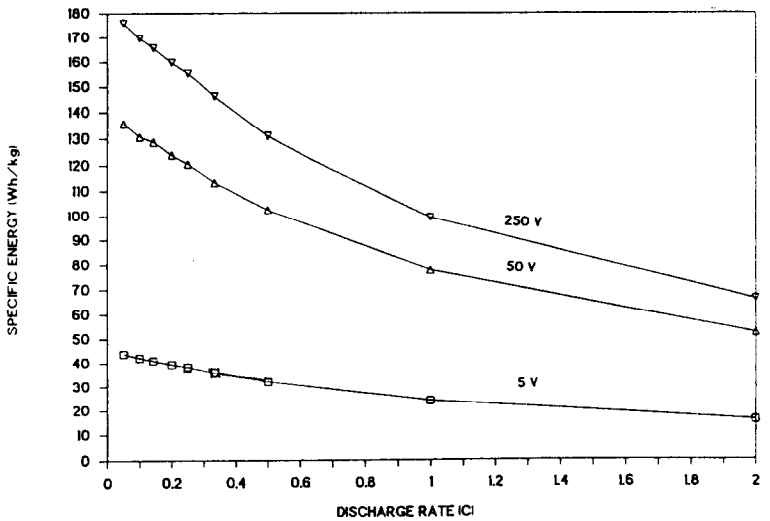


Fig. 5. The effect of battery discharge rate on the specific energy of 10 A h batteries.

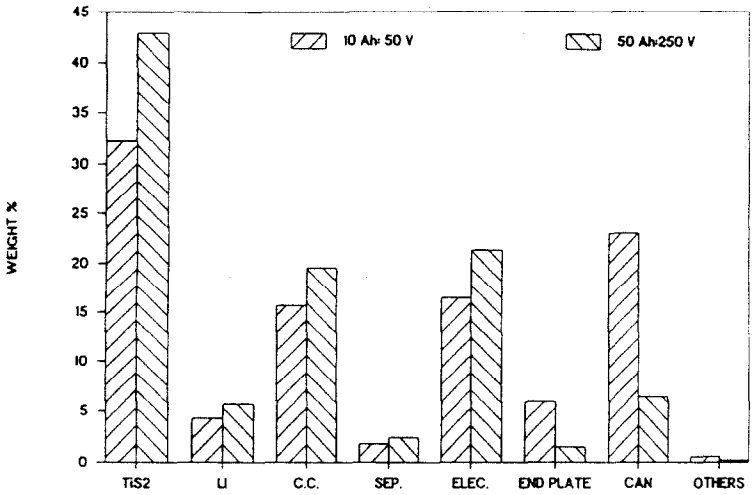


Fig. 6. The weight budget of various components of 10 A h, 50 V and 50 A h, 250 V Li/TiS_2 batteries; c.c.: current collector.

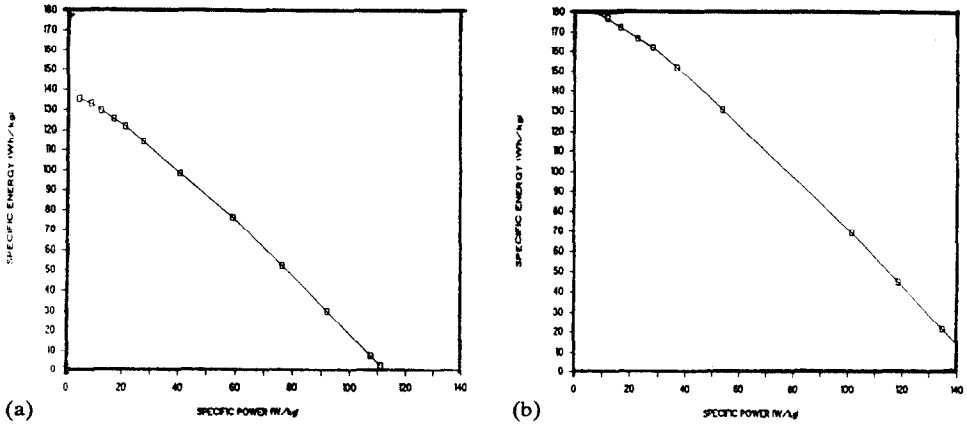


Fig. 7. Ragone plots of (a) 10 A h, 50 V and (b) 50 A h, 250 V Li/TiS_2 batteries.

Experimental bipolar Li/TiS_2 batteries

Typical discharge and charge curves of an experimental bipolar Li/TiS_2 battery are shown in Fig. 8. The shapes of these curves are similar to those of a single cell discharge and charge curves except that the battery voltage is a sum of three cells. The preliminary cycle-life data of an experimental (three-cell) bipolar battery is shown in Fig. 9. No capacity decline was observed from the 2nd to 15th cycle. The battery cycling was intentionally discontinued after the 15th cycle.

Figure 10 shows the discharge characteristics of the experimental bipolar Li/TiS_2 batteries at three different discharge rates. At 5 mA/cm^2 ($\sim$1.4 C), a theoretical cathode utilization of 30–40% was obtained. However, low utilizations (<5%) were noted at 2.8 and 5.2 C in continuous discharge. These results suggest that mass transport is the controlling factor of the battery performance during discharge. Further,

TABLE 4

Performance comparison between monopolar and bipolar 10 A h, 50 V, *C*/2 rate Li/TiS_2 batteries

	Monopolar design	Bipolar design	Improvement (%)
Specific energy (W h/kg)	71	99	39
Energy density (W h/l)	172	197	15
Specific power (W/kg)	29	41	41
Power density (W/l)	70	81	16

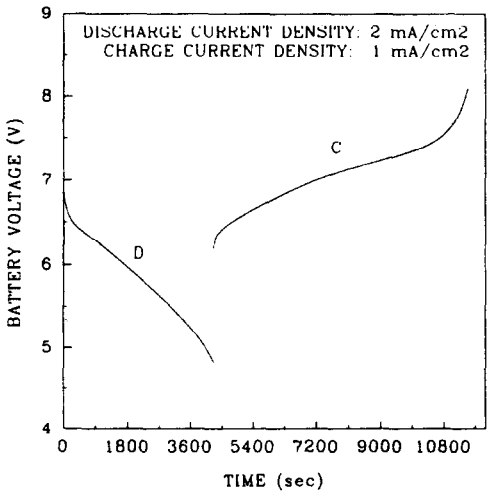


Fig. 8. The typical discharge and charge curves of an experimental bipolar Li/TiS_2 battery.

the mass transport is believed to be controlled by the Li transport. Figure 11 shows the discharge curve of an experimental bipolar battery at 5 mA/cm^2 (1.4 C) and with a 5 s pulse/5 s rest cycle. Higher theoretical cathode utilization (~60%) was achieved for this pulse discharge compared with the continuous discharge (30–40%). The increased cathode utilization during pulse discharge reflects the improvement of the mass transport of Li in the battery in this mode.

Further studies were carried out to identify the significance of the mass transport problem in the Li/TiS_2 batteries. Figure 12 shows the battery capacity during 5 s pulse discharge at 10 mA/cm^2 (2.8 C) with three different rest periods (5, 10, and 25 s). Significant improvements on the battery capacity were observed during discharge with longer rest periods. Approximately 60% improvement was obtained during pulse discharge with 25 s rest period. These results support the belief that Li mass transport is the limiting factor during high rate discharge. Two types of Li ion mass transport

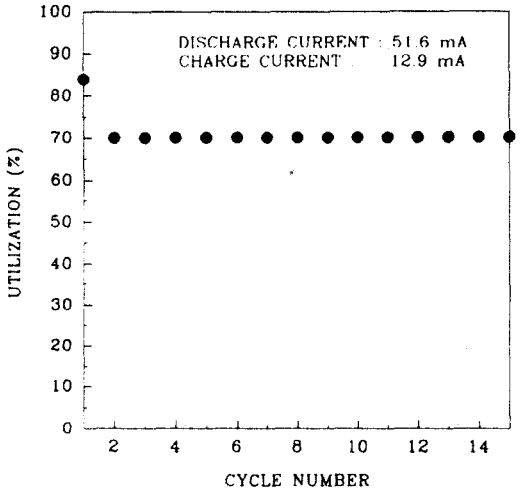


Fig. 9. Cycle-life data of an experimental (three-cell) bipolar battery.

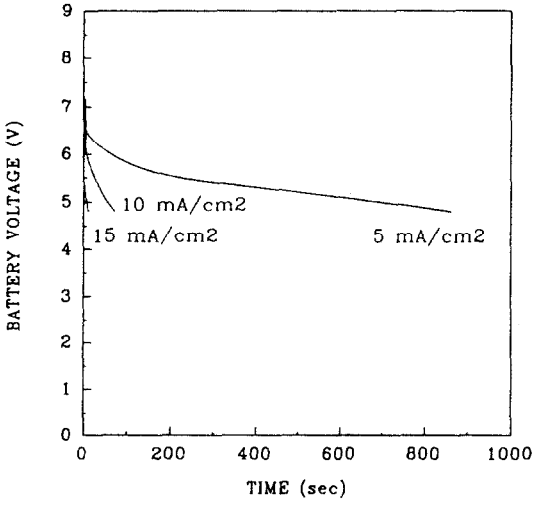


Fig. 10. Discharge characteristics of bipolar Li/TiS_2 batteries at different discharge rates.

limitations are involved in the discharge processes. The first is the Li ion transport in the electrolyte (especially in the cathode pore) and the second is the Li ion transport in the layers of TiS_2 material. Diffusion of Li ion in electrolyte and TiS_2 were studied earlier [7]. The results indicate that the Li diffusion in TiS_2 is the limited mass-transport factor.

The influence of pulse duration on battery discharge capacity was also studied. The results show a gradual decline in battery performance with increase in the pulse duration. The effect of current density and pulse duration on the cycle life will be investigated more fully in future work.

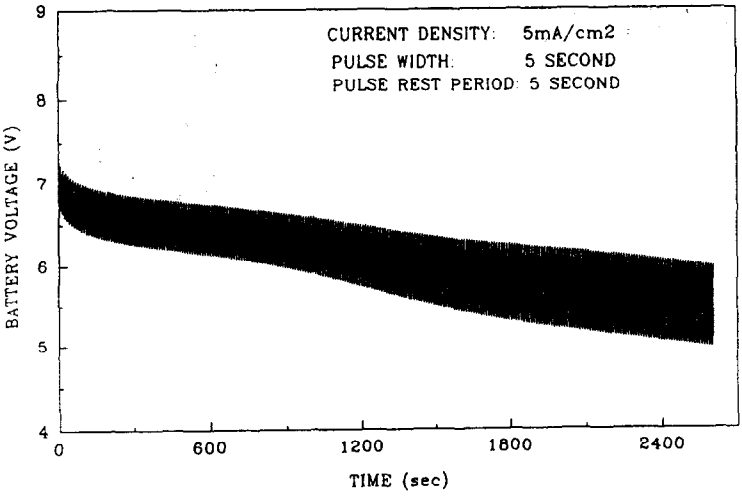


Fig. 11. A typical pulse discharge curve of a bipolar battery.

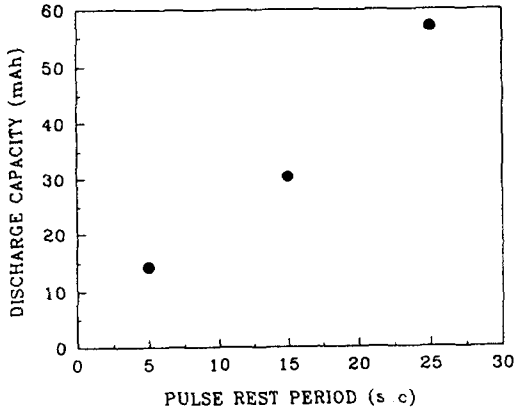


Fig. 12. Influence of rest period on battery capacity under pulse discharge; discharge current: 258 mA (10 mA/cm^2), pulse period: 5 s, and rest period: 5, 15 and 25 s.

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