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Capacity fade analysis of a battery/super capacitor hybrid and a battery under pulse loads – full cell studies

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Abstract

A detailed analysis of the capacity fade of a battery/supercapacitor hybrid and a battery alone has been carried out at 55 °C by discharging them at three different pulse rates. The applied peak current amplitudes were 5C (7 A), 3C (4.2 A), and 1C (1.4 A), respectively. The results indicated that for hybrids the pulse discharge run time was extended for all pulse discharge rates. The ohmic resistances estimated as a function of the pulse discharge rates were smaller for hybrids when compared with those for batteries. The variation of the ohmic resistance under pulse discharge with cycling, irrespective of the pulse discharge rate was smaller for hybrids than that for the batteries. The batteries and hybrids cycled at the lowest pulse discharge rate (high pulse discharge time) have larger capacity fade when compared with the capacity fade of the batteries and the hybrids discharged using higher discharge rates (low pulse discharge time). Impedance, cyclic voltammogram, and the rate capability studies were carried out on batteries cycled alone and on batteries cycled as part of the hybrid. The battery showed larger increase in the interfacial impedance with cycling when compared with the hybrid system.

1. Introduction

Hybrid energy storage devices are more efficient than a battery in supplying the total power for use in digital cellular phones, space communications, power distribution systems, uninterrupted power supply, electric and hybrid vehicles, portable computers and military applications [1]. The load in these systems is usually not a constant, but of the pulse type. A lithium ion battery has a high energy density of about 10^5 J/kg. However, it cannot meet high power demands when discharged at high currents. A lithium ion battery-super capacitor hybrid system is preferred over a lithium ion battery for higher rates of discharge due to the higher power density of an ultra capacitor ($\sim 10^6$ W/kg) compared to that of a lithium ion battery ($\sim$100 W/kg). Also, since the internal resistance of the super capacitor is smaller than that of the battery, the super capacitor shares the major part of the load current during high power demands, thus making the hybrid system more beneficial.

Dougal et al. have analyzed the interrelations between battery, ultracapacitor and the load in terms of their power and energy partitions [1]. Performance optimization of a battery-capacitor hybrid system has been recently studied by Sikha and Popov [2]. Characterization of a lithium ion battery-super capacitor hybrid using impedance measurements were done by Chu and Braatz [3]. Comparison between a battery-capacitor hybrid and a battery under pulse loads using Ragone plots was done by Holland et al. [4]. Capacity fade analysis of lithium ion batteries at elevated temperatures under constant current discharge has been done by Ramadass et al. [5, 6]. This explains the high rate of capacity loss with cycling at temperatures above room temperature. High temperature operation of lithium ion batteries is observed in modern electronics where they are discharged under temperatures up to 60 °C. In recent literature, experimental and theoretical work has been reported on the performance of lithium ion batteries under constant current discharge at room and elevated temperatures [7–9]. However, a detailed analysis of the capacity fade of the battery coupled with the capacitor under pulse type of loads has not been presented in literature.

The objective of this work was to study the capacity fade of battery-super capacitor hybrid systems and single batteries cycled up to 400 cycles. The capacity fade of both systems was investigated by using three different discharge pulse protocols at an elevated temperature of 55 °C. Capacity check, rate capability studies, electrochemical impedance analysis and cyclic voltammetric studies were also carried out for both hybrid and battery systems.

2. Experimental

2.1. *Full-cell studies*

The hybrid system in our experiments consisted of a single Sony US 18650 lithium ion cell with a rated capacity of 1500 mA h in parallel with a set of Maxwell PC super capacitors with an effective capacitance of 50 F. Two 100 F capacitors were connected in series to obtain a 50 F capacitance with a capacitor configuration index [2] of 0.5. Clubbing the two capacitors in series approximately gives the equilibrium potential of a single lithium ion battery.

The hybrids were cycled at an elevated temperature of 55 °C. The hybrid system was charged to 4.2 V using the conventional constant current – constant voltage (CC-CV) protocol. Constant current charging was carried out at 0.7 A or C/2 rate and subsequently the voltage was held constant at 4.2 V until the current dropped to 50 mA. The hybrids were discharged at three different pulse rates with peak current amplitudes of 5C (7 A), 3C (4.2 A), and 1C (1.4 A), respectively. Here C refers to the capacity of the hybrid system and is equal to 1.4 A h for our system. The capacity of the capacitor is almost negligible. The duty ratio of the discharge pulse and the pulse frequency were fixed at 0.1 and 1 Hz, respectively. The cut-off voltage on discharge for the lithium ion battery in this study is 2.5 V. Below this voltage there is no intercalated lithium available at the carbon electrode for discharge. The same set of protocols were applied to the battery alone systems.

An Arbin BT-200 battery cycler was employed for cycling, rate capability and cyclic voltammetry studies. The high cycling temperature of 55 °C was maintained using a Tenny Model T6S environmental chamber. A Solatron SI 1255 HF Frequency Response Analyzer and Potentiostat/Galvanostat Model 273A were used for the electrochemical impedance studies for both the fresh and the cycled Sony 18650 cells.

Capacity checks were done for both the fresh and cycled cells which were part of the hybrid by charging them using the CC-CV protocol as mentioned before, followed by a constant current discharge at C/2 rate. All capacity checks were done at room temperature, and for the hybrid systems the battery was separated from the capacitor before the capacity check was done. This was done to make sure that the capacity fade of the battery and the hybrid systems were compared based on the degradation of the battery in both systems. Rate capability and cyclic voltammetry studies were carried out for both the fresh and the cycled lithium ion cells used in the hybrid system. Rate capability analysis was done by charging the lithium ion cells, both fresh and those cycled as part of the hybrids, using a CC-CV protocol and then discharging at constant currents of C/8, C/4, C/2 and C rates. Cyclic voltammetric studies were carried out at both low and high scan rates of 0.05 and 0.2 mV s^{-1}, respectively. Electrochemical Impedance Spectroscopy (EIS) was done for both the fully charged and discharged states of the battery. A sinusoidal wave perturbation with amplitude of 5 mV was applied over a frequency range of 0.1 Hz–0.1 MHz to obtain the impedance spectra. For comparison, the above outlined experiments were also carried out on a Sony US 18650 lithium ion battery alone system, both fresh and cycled under the same protocol.

The ohmic resistance at each pulse was calculated by dividing the voltage drop at that pulse by the amplitude of the pulse discharge current. Since there is not a large variation in the ohmic resistance at each pulse during an entire discharge at a given pulse rate, the average of the ohmic resistance during an entire pulse discharge at each rate is used in our studies.

3. Results and discussion

3.1. *Discharge characteristics*

Table 1 gives the percentage capacity fade at different cycle numbers for both the battery and hybrid cycled at three different pulse discharge rates. As shown in Table 1 at 200 cycles, the battery in the hybrid always had higher capacity fade than the battery alone system irrespective of the discharge rate used. The systems cycled at higher pulse discharge rates showed lesser capacity fade than those cycled at lower pulse discharge rates, irrespective of whether it is a battery or a hybrid system. However with further cycling, the hybrids which were cycled at low pulse discharge rates show better performance when compared to that of the battery alone system.

The capacity fade of the 1C battery after 300 cycles is 45.5%, while the highest capacity fade after 400 cycles of the battery in the 1C hybrid is 47.7%. Since the rate of capacity fade of 1C battery is the highest, its capacity fade at 400 cycles will be higher than that of the battery in the 1C hybrid at the same cycle number. The capacity

Table 1. Capacity fade (%) of the battery in the hybrid and the battery under pulse discharge

Cycle number	Capacity fade (%)					
	Battery (pulse discharge rate)			Battery in the hybrid (pulse discharge rate)		
	1C	3C	5C	1C	3C	5C
100	11.232	2.527	1.126	15.696	11.332	10.288
200	27.345	8.304	4.383	27.808	16.275	14.897
400	45.484 (at 300 cycles)	26.506	9.087	47.724	30.153	35.282

fade of 1C battery is higher than that of 3C and 5C batteries, which is due to larger run time at low pulse discharge rates. This phenomenon is further enhanced when small duty ratios were used to discharge the battery. The capacity fade of the hybrid discharged at a pulse rate of 1C at 55 °C is higher than the capacity fade of the hybrid discharged at 3C and 5C rates. The battery cycled at a pulse discharge rate of 1C has the highest capacity fade followed by the one at 3C and then the 5C battery. The 3C battery shows a capacity fade of 8.3% at 200 cycles. The capacity fade of the battery cycled at a pulse discharge rate of 5C is as low as 9% even at 400 cycles. The results indicated that the battery in the hybrids cycled at pulse discharge rates of 3C and 5C have similar capacity fade values.

Figure 1a and b show the pulse discharge run time as a function of cycle number estimated for hybrids and batteries, respectively. Higher capacity fade were observed in the hybrids and batteries alone discharged at 1C pulse rate when compared to those discharged at 3C or 5C pulse rates which is due to the higher pulse discharge run time in the case of 1C than at 3C or 5C. Literature suggests that the capacity fade under constant current discharge of 1C is smaller than that at constant current discharge rates of 3C or 5C [10]. The reason for the observed discrepancies can be explained by taking into account that under pulse loads the difference in the total cycling time between 1C and the higher rates of 3C and 5C is much higher than that under constant current discharge, especially at low pulse duty ratio used in the present work. The estimated differences in the total cycling time and the contribution from the self discharge to the total capacity fade are discussed below in detail.

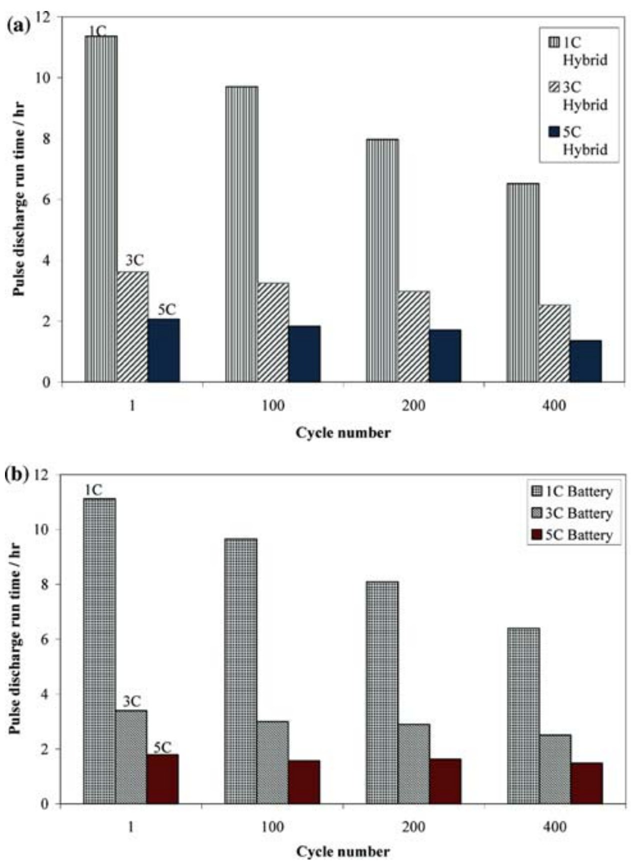

Fig. 1. Pulse discharge run time (h) vs. cycle number for the (a) hybrids; and (b) batteries.

Note, that the difference in run time between 3C and 5C rates is not as high as that observed between 1C and 3C rates. This explains as to why only small differences were observed in capacity fade values for hybrids discharged using 3C and 5C rates.

When the pulse discharge run time is larger, the system is under strain due to cycling for a longer period at 55 °C. This results in higher capacity fade at 1C rate than at 3C or 5C rates due to larger volumetric strain. Also, at low pulse discharge rates, both hybrids and batteries will be discharged to lower end of discharge voltage than the corresponding systems discharged at high rates. Accordingly, the charge time of the battery in the hybrid and the battery cycled alone also will be larger for 1C than for the 3C and 5C rates.

It has been reported in the literature that most of the side reactions occur during charging, especially during the CV part [11] which explains the higher capacity fade of 1C rate hybrids and batteries than the higher rate systems. Moreover, the duty ratio of the discharge pulse is very low and so the overall time for which the cells are being cycled at lower pulse discharge rates for both systems would be much higher than those cycled at higher pulse discharge rates. In other words, when larger cycle numbers are reached, the cumulative time from the beginning of cycling for the cells discharged at low rates will be too large that irreversible capacity losses due to self discharge should also be accounted. According to Ramasamy *et al.* lithium ion batteries exhibit a notable irreversible capacity loss during storage [12]. The authors have further stated that higher temperature accelerates the degradation of the cells. Johnson and White [13] found that at room temperature, the self discharge of Sony 18650 cells with coke as the anode material is 2.5% for 1 month. In the current work, since pulse discharge is employed, it takes approximately 6 months for the 1C rate battery and 7.5 months for the 1C hybrid to complete 300 and 400 cycles, respectively at 55 °C. Thus, it is clear that self-discharge of the lithium ion cells is even more significant in the present work because of elevated temperature. Table 2 shows the total cycling time for the 400th cycle (total charge time and the pulse discharge time for the 400th cycle) for the case of the batteries and hybrids for all three rates of pulse discharge. This table shows that at 400 cycles, the cycling time of the 1C battery (300 cycles only in this case) and the 1C hybrid is higher than the corresponding system cycled at 3C pulse discharge rate by 3.7 h and that at 5C rate by approximately 4.85 h. The large difference in cycling time between the 1C and the higher rates in one cycle itself, explains the need to consider the irreversible capacity losses due to self discharge of the cells at low pulse discharge rates under prolonged cycling especially at elevated temperatures. Moreover

Table 2. Total cycling time (total charge time and the pulse discharge time) of the hybrids and batteries for the 400th cycle

Pulse discharge rate	Total cycling time for the 400th cycle (h)	
	Battery	Hybrids
1C	8.28 (300 cycles)	8.42
3C	4.56	4.63
5C	3.49	3.51

the total charge time trend (data not given) between the battery in the hybrid and the battery, both discharged at a pulse rate of 1C, is in agreement with the capacity fade observed between these two systems. The pulse discharge run time and its influence on the charge time and the length of CV part in the total charge time can be used to explain the capacity fade observed in other cases as well.

Besides the fact that it has been suggested in literature [1, 2] that the performance of the battery could be improved when coupled with a supercapacitor, still sufficient data have not been published on the capacity fade of hybrids and batteries especially at elevated temperatures. It can be seen from Table 2 that hybrids have a slightly greater total cycling time for the 400th cycle than the batteries discharged with the same pulse amplitude. This difference in cycling time between hybrid and battery has been observed to be even greater during the initial stages of cycling. So the effect of temperature on the factors contributing to capacity fade is pronounced for a longer time in the case of the hybrids. This phenomenon also explains the higher capacity fade of the hybrids when compared to the batteries cycled alone which is observed in most cases.

Figure 2a, b and c show for the first cycle, the pulse discharge curves for both battery and the hybrid configuration at 1C, 3C and 5C rates, respectively. Since the voltage drop is lesser in a hybrid than in a battery alone configuration during a pulse discharge, the hybrid stays at a higher SOC than the battery throughout the discharge. This difference between a battery and a hybrid is higher for a higher rate of pulse discharge. It is worth mentioning here that the difference in capacity fade is also higher between the 5C battery and the 5C hybrid than between the ones cycled at lower pulse discharge rates. Moreover, besides the fact that supercapacitor has very long cycle life, self discharge of the supercapacitor can take place even when the system is being cycled. Self-discharge of the supercapacitor becomes significant at elevated temperature [14], especially when the time for which it remains at elevated temperature is large i.e. at low rates of pulse discharge and also at large cycle numbers. This would greatly affect the current sharing ability of the super capacitor under prolonged cycling conditions. This explains why the hybrids do not show a lesser fade than batteries especially at higher pulse discharge rates. It can also be inferred from Table 2 that lower the pulse discharge rate, the higher is the extension of run time in hybrids as compared to batteries, especially at low pulse duty ratios. However, this increase in run time in a hybrid when compared to its corresponding battery at 400 cycles is less than even 10 min because the load sharing capability of the supercapacitor has decreased significantly at 400 cycles. This decreased capability of the supercapacitor has to be more pronounced at 1C rate than at 3C or 5C rate due to its higher total cycling time. This explains the higher fade of the hybrid systems cycled at a pulse discharge rate of 1C than that done at 3C or 5C.

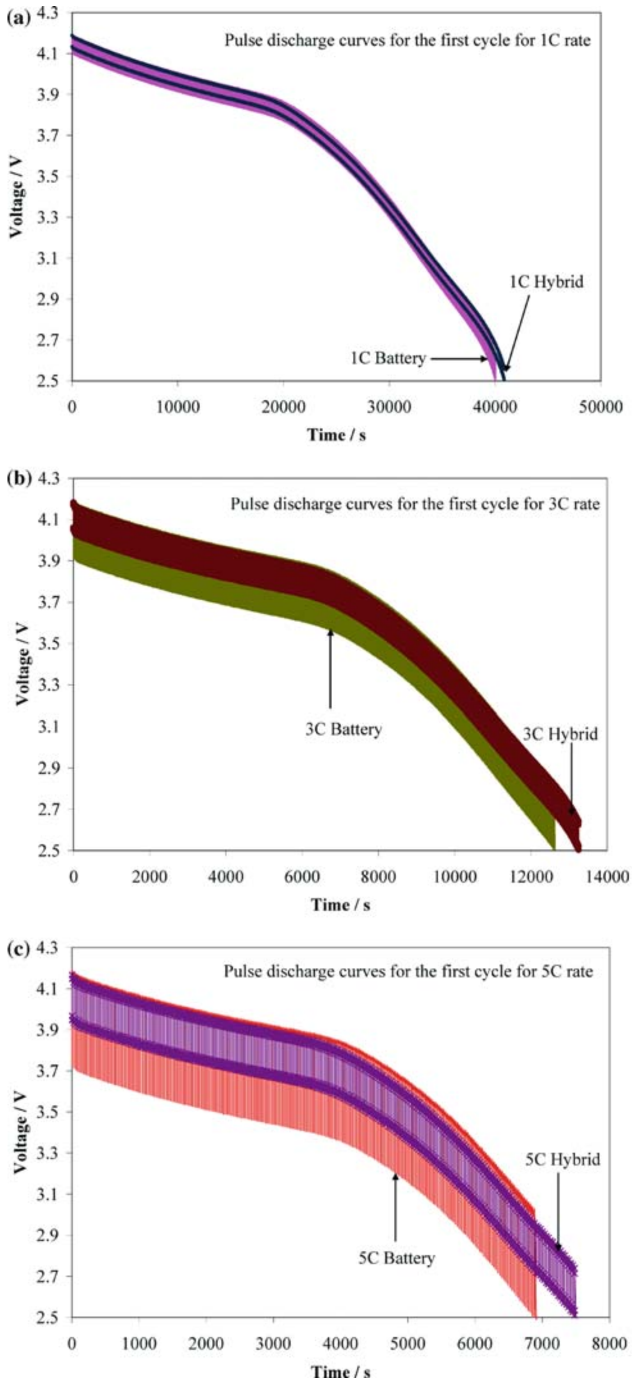

Fig. 2. Pulse discharge curves for the first cycle for the battery and hybrid cycled at (a) 1C rate; (b) 3C rate; and (c) 5C rate.

Figure 3a, b and c show the discharge curves obtained by the capacity check test of the battery in the hybrid and the battery cycled at pulse discharge rates of 1C, 3C, and 5C respectively. The lack of any potential plateau indicates the use of coke based anode [13]. It can be seen that with cycling, the initial drop in the voltage profile increases. This sudden drop in potential at the initial portion of the discharge curve is due to the ohmic cell resistance. The voltage drop during discharge also decreases the available energy of the cell drastically because of lower voltage profile of operation. The high initial voltage drop of the battery in the hybrid as compared to its corresponding battery observed during a capacity check supports the higher fade of the hybrids when compared to the corresponding batteries. The higher voltage drop observed for 1C rate batteries and hybrids under prolonged cycling as compared to the 3C and 5C rate batteries and hybrids supports the higher fade of 1C hybrids and batteries.

3.2. *Electrochemical impedance spectroscopy*

Impedance measurements were done for full cells at both, fresh and cycled conditions on the batteries which were cycled alone and as a part of the hybrid system. The Nyquist plot of a fresh Sony 18650 Lithium ion cell comprises of an inductive tail in the high frequency region, which is usually ignored when the analysis of the impedance spectrum with cycling is done [15], followed by two semicircles with different magnitudes at low and mid frequency range. The impedance loops at medium and low frequencies are attributed to the interfacial resistances [16] . Finally, a tail part is observed in the very low frequency region which is usually attributed to the diffusion impedance.

Ohmic cell resistance is the high frequency intercept of the Nyquist plot. The ohmic resistance of the fresh cell is found to be 0.15 ohms at zero state of charge (0 SOC) and 0.14 ohms at 100 SOC, which implies that ohmic cell resistance does not vary much with the state of charge. The ohmic cell resistance increases slightly with cycling. The difference between the ohmic cell resistances at 100 and 400 cycles is of the order of 0.005 ohms. The same order of magnitude difference is obtained from the ohmic resistance under pulse discharge studies that will be discussed later. Ohmic cell resistance includes the electrolyte resistance, electrode bulk resistance, separator resistance, etc. in series [16].

It is desirable to determine whether there is an increase in interfacial resistance with cycling which could be correlated to the capacity fade. Since ohmic resistance is constant with the state of charge, from the Nyquist plots at 0 SOC and 100 SOC, it can be inferred that non-ohmic resistances (charge transfer resistance) are dependent on the SOC of the cell. This is in accordance with literature which suggests that ac impedance is a strong function of SOC [10]. The impedance of the cell in the fully charged state is observed to be lower than the impedance in the fully

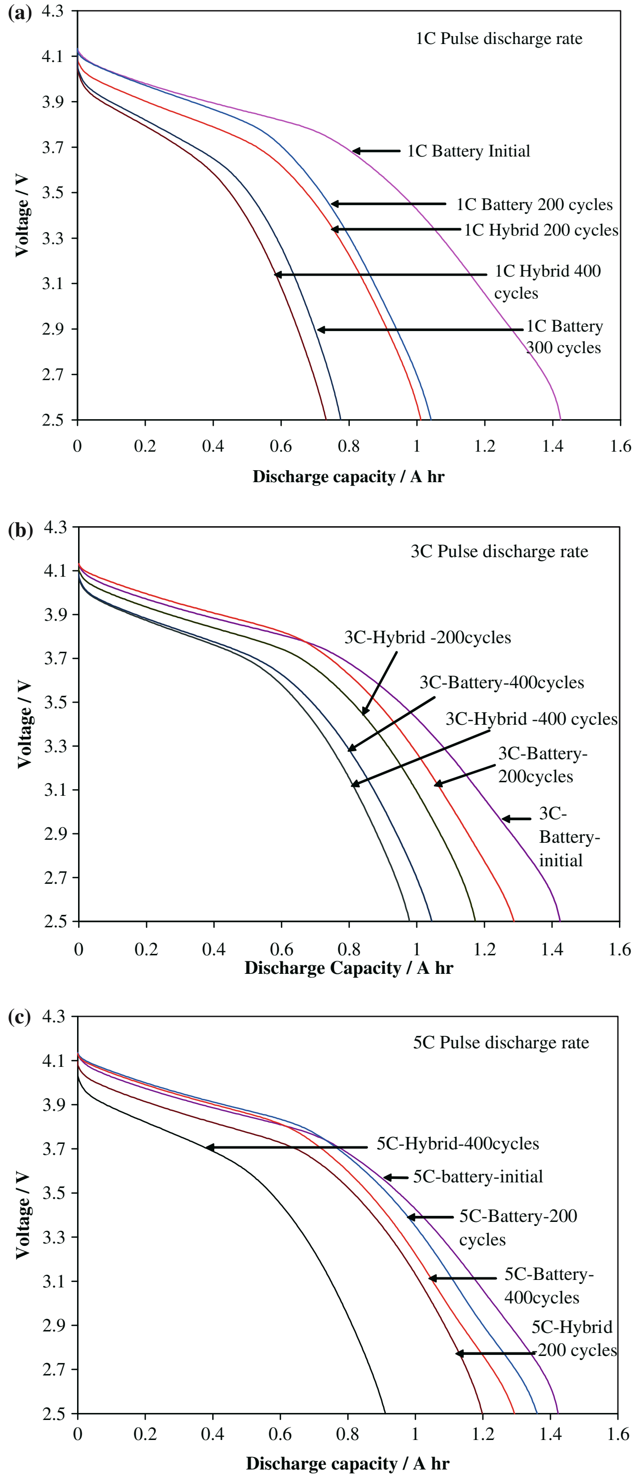

Fig. 3. Discharge curves of the battery in the hybrid and the battery cycled at a pulse discharge rate of (a) 1C; (b) 3C; and (c) 5C.

discharged state (figure not given) and this is also in agreement with literature [17]. Besides the fact that the magnitude of the impedance values differs with SOC, the trend in impedance remains the same at both 0 SOC and 100 SOC.

Figure 4a, b and c show the Nyquist plots at fully discharged state, both for the battery and the battery in the hybrid which were cycled at pulse discharge rates of

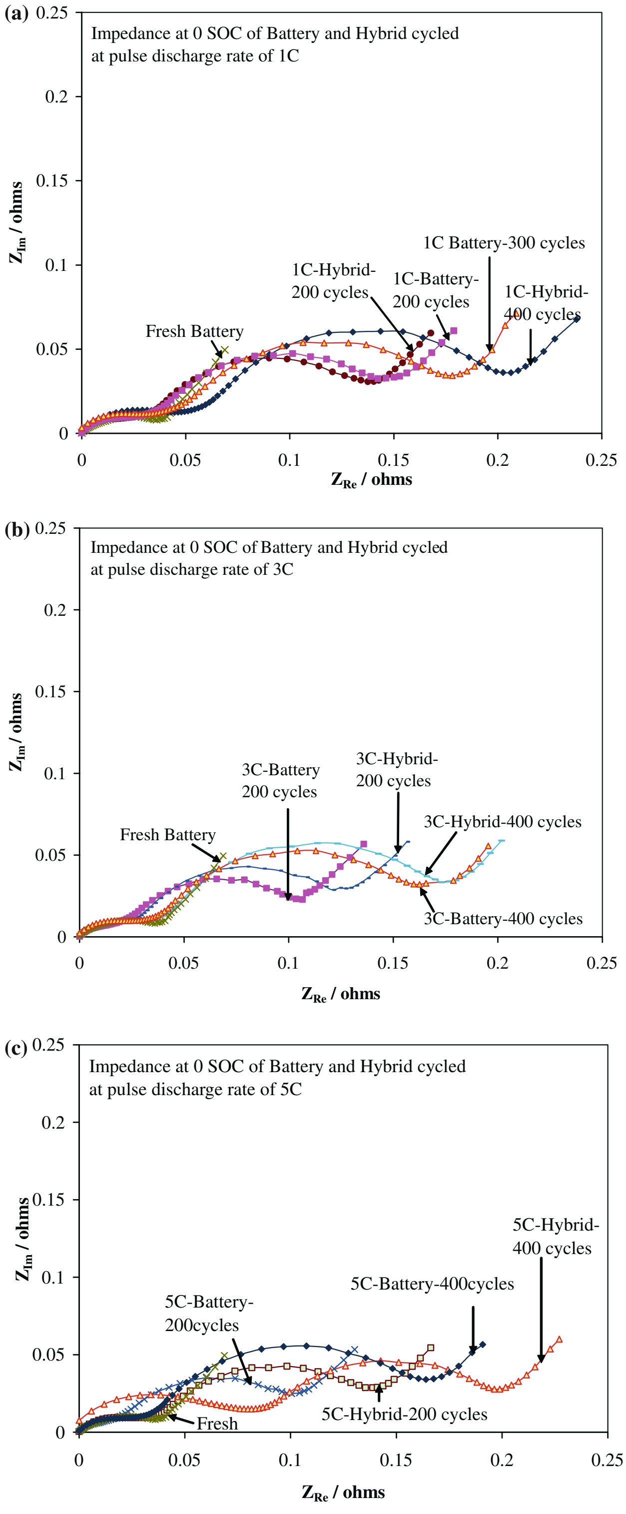

Fig. 4. Impedance at 0 SOC of the battery in the hybrid and the battery cycled at a pulse discharge rate of (a) 1C rate; (b) 3C rate; and (c) 5C rate.

1C, 3C, and 5C respectively. As shown in these figures, the semicircle at medium frequency is smaller than that at low frequency. Figure 4 shows that the size of the semi circle at the medium frequency (the first from the origin) remains almost constant and becomes slightly prominent with cycling. The size of the semi circle at low frequencies (second loop) varies distinctly with cycling. Thus, it can be inferred from Figure 4 that the ac impedance increases with cycling for both the battery alone and the battery in the hybrid irrespective of the pulse discharge rate. This indicates an increase in electrode resistance with cycling in both cases. Figure 4a shows that at 200 cycles the impedance of the battery is slightly higher than that of the battery in the hybrid for the case of 1C pulse discharge. This is consistent with the high rate of capacity fade of the 1C battery. It is seen that at 200 cycles, the battery cycled at 5C rate has the least impedance. The impedance of 1C battery at 300 cycles is less than that of the 1C hybrid at 400 cycles. The results are consistent with the capacity fade values for these systems. If the 1C battery had been cycled up to 400 cycles, its impedance might have been higher than that of the 1C hybrid and thus could have substantiated the high rate of capacity fade of 1C battery. The ac impedance of the batteries in the 1C hybrid at 400 cycles is higher than that of the batteries in the hybrids cycled at pulse discharge rates of 3C and 5C. The 1C battery has higher ac impedance at 300 cycles itself than do the 5C and 3C battery at 400 cycles. The results are in agreement with the capacity fade data presented in Table 1. It can be also seen that the impedance of the battery in the hybrids is higher than that of the corresponding batteries, irrespective of the pulse discharge rate at all cycle numbers. This supports the higher capacity fade of the hybrids as compared to that of the batteries.

The interfacial resistances observed in impedance spectra may not be directly related always to the capacity fade, and hence the trend seen in impedance need not always match that of the capacity fade.

It is thus possible for a system to have a high discharge capacity as well as a high interfacial resistance [15]. The continuous increase in the interfacial resistances with cycling will indicate that the available capacity decreases continuously due to the film formation process which consumes Li^+. Aurbach et al. claim that the surface reaction on both the electrode surfaces increases the impedance of the electrodes and thus increase the overall battery resistance and thus shortening the capacity upon cycling [18]. Hence it should be noted that a direct correlation between the increase in interfacial resistance of the battery and the discharge capacity fade cannot be always drawn, but this impedance data could be used as a tool to investigate the extent of film formation which indirectly result in capacity fade.

3.3. *Cyclic voltammograms*

Figure 5a, b and c show the cyclic voltammograms of the battery in the hybrid and the battery alone discharged at 1C, 3C, and 5C rates respectively for both fresh and cycled cases, at a low scan rate of 0.05 mV s^{-1}. The forward scan is associated with the charge process and the reverse scan with the discharge process of the battery [17]. The magnitude of the peak current

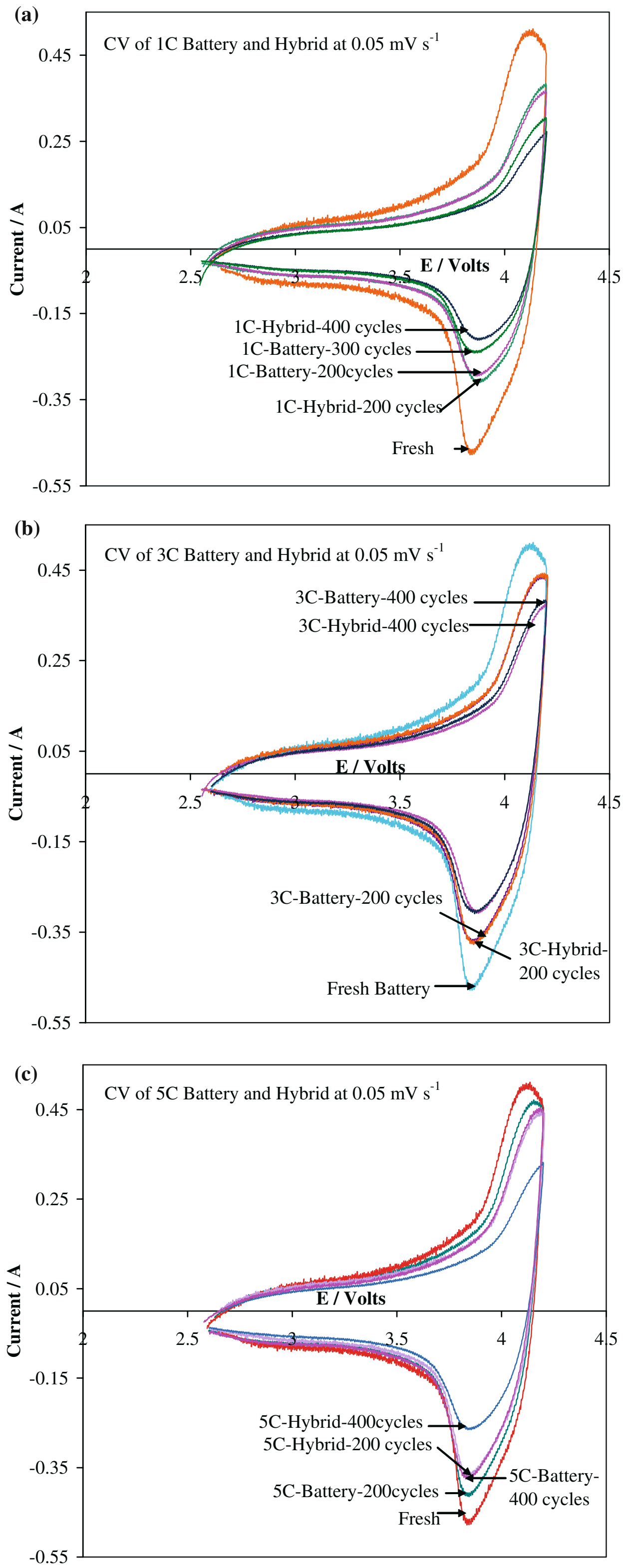

Fig. 5. Cyclic Voltammogram of the battery in the hybrid and the battery cycled at a pulse discharge rate of (a) 1C; (b) 3C; and (c) 5C (scan rate: 0.05 mV s^{-1}).

indicates the extent of available active material in the battery. The results indicated that for a fresh battery the peak current or the intercalation peak occurs at approximately 4.1 V. The intercalation is almost complete when the system is scanned forward until 4.2 V and there is a quick shift to negative current as soon as the reverse scan is started . However, for the case of the cycled cells the intercalation peak shifts close to 4.2 V, which results in positive values of the current to be still observed when the reverse scan starts. This is due to increased resistance in the cycled cells, which shifts the intercalation peak further right, and hence not all the intercalation sites are occupied by active material filled during the forward scan. As a result, during the start of the reverse scan, intercalation still occurs , indicating positive current before it changes the polarity to negative values.

The cyclic voltammograms in Figure 5 also reveal that the peak currents decrease with cycling for both the battery and the battery in the hybrid irrespective of the pulse discharge rate. This is because of the loss of cyclable lithium with cycling, which results in lower peak currents. The peak current of the battery at 200 cycles and 400 cycles is greater than that of the battery in the hybrid at the corresponding cycle numbers when both are cycled at a pulse discharge rate of 5C. This implies the active material degradation with cycling in the battery in the hybrid is greater than that in the battery alone at 5C pulse discharge rate. This is consistent with the capacity fade data. At 1C pulse discharge rate, the peak current of the battery in the hybrid is higher than that of the battery at 200 cycles. This is also consistent with the capacity fade data, wherein the capacity fade of the 1C battery closely approaches that of the 1C hybrid at 200 cycles. At 200 cycles, the highest peak current is that of the 5C battery and it has the least capacity fade. The peak current trend at 400 cycles exactly matches that of the capacity fade i.e. the peak current of the 1C battery at 300 cycles is smaller than those of the 3C and 5C battery at 400 cycles. This is an indication of the extent of active material deterioration in the 1C battery, which leads to such high capacity fade. The capacity fade of 1C battery at 300 cycles is lesser than that of the 1C hybrid at 400 cycles which is reflected in the higher peak current of the former as compared to that of the latter. The results indicated that for a given pulse discharge rate, the greater the cycle number, the greater is the electrode deterioration and the smaller should be the peak current.

3.4. *Rate capability studies*

The rate capability of a lithium ion battery is the maximum continuous or pulsed output current it can provide [5]. Figure 6a and b show the normalized discharge capacity of the battery and the battery in the hybrid, cycled at all three pulse discharge rates, at 100 and 400 cycles, respectively. The normalized discharge capacities were obtained by dividing the actual discharge capacity in each case by the discharge capacity obtained from a fresh cell discharged at C/8 rate.

The fresh cell shows a better performance than that of any of the cycled ones. At 100 cycles, the battery in the 1C hybrid shows the worst performance, followed by the 1C battery and the battery in 3C hybrid. This is in agreement with the capacity fade at 100 cycles. The performances of the other systems are better than the above three at 100 cycles. At 400 cycles, 5C battery shows the best performance among all cycled ones because it has the least capacity fade. The overall performance trend matches with that of the capacity fade trend at 400 cycles.

Rate capability can be obtained from the slope of the curves in Figure 6a and b. It is inferred that for any system, rate capability decreases with cycling. However, at a particular cycle number, the slope does not vary much among batteries and batteries in the hybrids cycled at various pulse discharge rates. Therefore it can be concluded that at a given cycle number, the rate capability in the present work does not reflect the difference in capacity fade observed between hybrids and batteries cycled at different pulse discharge rates. Rate capability can only support the capacity fade with cycling.

The rate capability of the cell decreases with increasing the cell ohmic resistance. The effect of ohmic resistance and other cell resistances are negligible at a very low discharge rate such as C/8, however they become more pronounced at high rates.

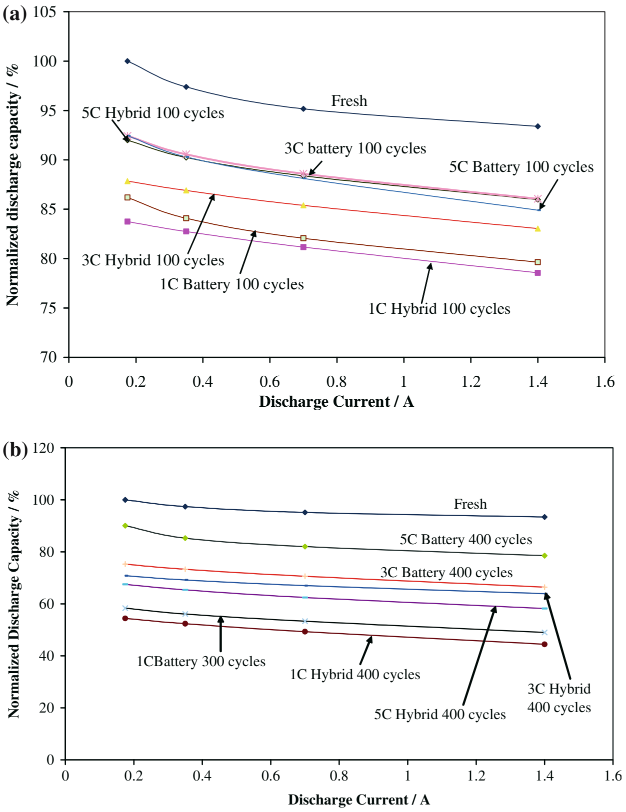

Fig. 6. Rate capability studies of the battery in the hybrid and the battery alone cycled at pulse discharge rates of 1C, 3C, 5C at (a) 100 cycles; and (b) 400 cycles.

3.5. *Ohmic resistance during a pulse discharge*

Figure 7a, b and c present the ohmic resistances as a function of the pulse discharge capacity at pulse discharge amplitudes of 1C, 3C, 5C, respectively. The results are summarized for both the batteries and the hybrids at different cycle numbers. Since in a hybrid system, the capacitor shares a major part of the pulse load, the ohmic resistance at any cycle number is less for a hybrid than that for a battery at any rate of pulse discharge. Due to high ohmic resistance, the batteries reach the cut off voltage of 2.5 V quickly whereas the

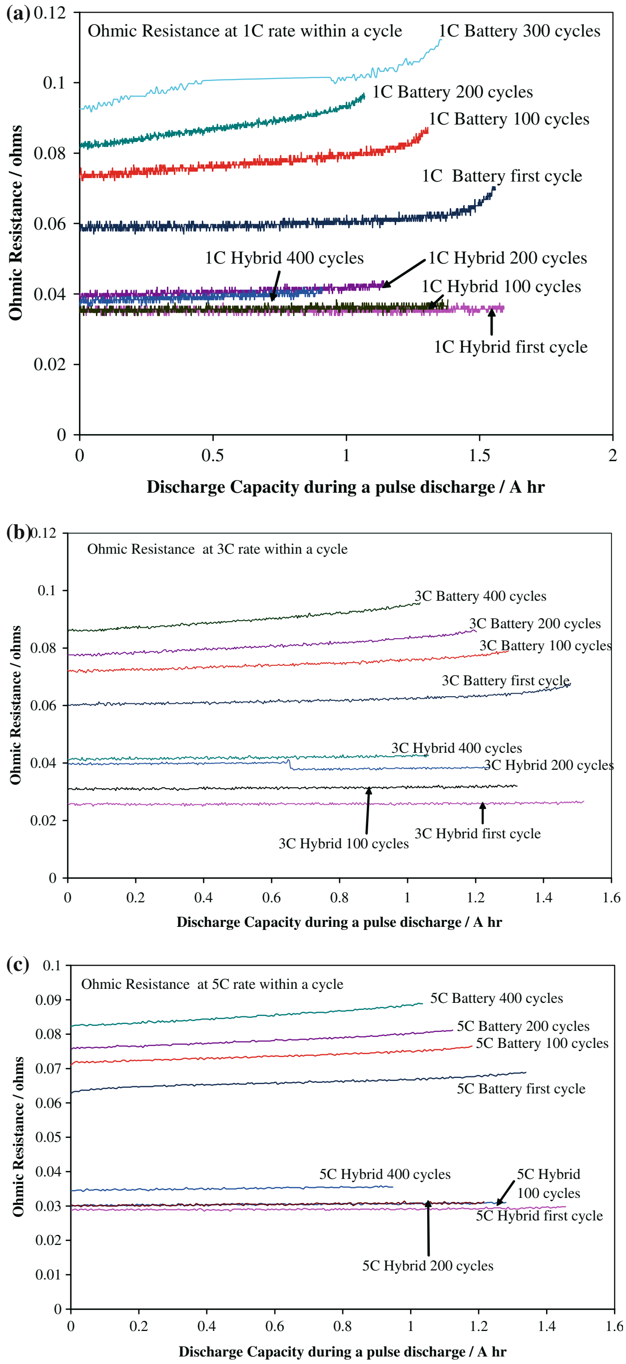

Fig. 7. Ohmic resistance during a pulse discharge vs. the pulse discharge capacity for battery and hybrid cycled at the pulse discharge rates of (a) 1C; (b) 3C; and (c) 5C.

hybrids take relatively longer time to complete the pulse discharge step in each cycle. Hence, the pulse discharge run time of the hybrid is higher than that of the battery as inferred from Figure 2. Figure 7 shows that the ohmic resistance increases only slightly with cycling for both the battery and the hybrid. It can be seen from Figure 7 that the variation in the ohmic resistance with cycling is less in hybrids than in the batteries, irrespective of the pulse discharge rate. It can also be inferred from Figure 7a, b and c that the increase in ohmic resistance of the 1C battery in the initial stages of cycling is significantly higher than that of the batteries cycled at 3C and 5C rates .This supports the higher capacity fade of the 1C battery among all three rates.

4. Conclusions

The capacity fade of the hybrid and the battery was studied at 55 °C under three different pulse loads. Impedance, cyclic voltammogram, and rate capability studies were carried out at different cycle numbers on batteries cycled alone and also on batteries cycled as part of the hybrid. At higher cycle numbers and at higher pulse discharge rates, the battery performs better than the hybrids. However the hybrid performs better than the battery at higher cycle number when both are cycled at a low pulse discharge rate.

The impedance is higher for the hybrids than for the corresponding batteries irrespective of the pulse discharge rate. A higher capacity fade of the hybrids than that of the corresponding batteries have been seen at all three rates. The results indicated that the active material is lost in film formation that leads to high interfacial impedance. The interfacial impedance supports the capacity fade data. Rate capability losses increase with cycling which is in agreement with the observed increase in capacity fade with cycling.

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