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Performance Evaluation of *Mg-AgCl* Batteries for Underwater Propulsion

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ABSTRACT

Magnesium-silver chloride seawater activated reserve pile-type battery was exclusively used in all underwater vehicles as a source of power due to its high energy density and power density. Various tests have been conducted on fully assembled battery to test its performance, suitability and compatibility. However, it is also essential that the battery is subjected to failure mode studies to understand the limitations of the battery and to analyse the vehicles performance under such situations. Various possible failure modes that the battery might experience during its usage as propulsion source in the underwater vehicle are identified, and the performance evaluation of scaled down model (10-cell module) of the battery has been carried out in the laboratory. The results are discussed to understand the electrochemical system and its effect on the overall performance of the vehicle. It has been observed that while some failure modes were found to affect the vehicles' performance adversely, only some failure modes are detrimental to the vehicle's performance.

1. INTRODUCTION

Magnesium-silver chloride (*Mg-AgCl*) seawater activated reserve pile-type batteries are developed for underwater application in general, and for underwater propulsion, in particular, because of the highest energy density and power density offered by this battery system along with very high discharge rate capability compared to any other known battery. During the developmental process while *AgCl* was the only cathode material used, magnesium alloys of different compositions are used to increase cell voltage and reactivity. These include: AZ-31, AZ-61, AP-65 and MTA-75 alloys of magnesium. Seawater is used as electrolyte in these batteries, rather exclusively. However, unlike normal cases where the batteries are filled with electrolyte, here the electrolyte has to flow through the battery continuously. This dynamic flow of electrolyte is necessary (i) to remove the heat generated due to corrosion of magnesium alloy anode with seawater, (ii) to remove the sludge formed by the reaction of seawater with the anode (both during corrosion and current generating reaction, which otherwise could stiffle the discharge reaction by blocking the active surface area of the plates), and (iii) to remove hydrogen gas generated due to corrosion of the anode, as the buildup of gas bubbles on the electrode surface affects the performance of the battery.

The performance of the battery is dependent on the electrolyte characteristics. The electrolyte flow rate, its salinity and temperature are the three parameters which influence and control the performance of the battery directly. Effect of variation of each of these parameters on the

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performance of the battery can be studied in the laboratory and optimised. Hence, the batteries are tested and evaluated in the laboratory by preparing synthetic seawater, simulating the actual seawater salinity and temperature, and pumping it through the battery at given fixed flow rates.

During development and evaluation of the underwater vehicle at sea, using this *Mg-AgCl* seawater battery, the performance characteristics of this propulsion battery too were generated. As the discharge characteristics of the battery determines the propulsion characteristics of the vehicle, it becomes essential to evaluate the performance of the battery under various test conditions. This should include the possible failure mode tests also, which are expected to occur during actual sea trials in the abnormal situations. As testing on full battery was not economical, a scaled down model was subjected to laboratory testing and evaluation, simulating various possible failure modes the battery may encounter during its actual usage in the underwater vehicle as a propulsion power source.

Different possible failure modes which might occur during actual usage of the battery during sea tests were visualised. The various failure modes were considered and tests conducted on the 10-cell modules to understand the electrochemical behaviour of the battery. These were:

(a) With normal electrolyte salinity, temperature and flow rate, the results of which were used for reference and comparison

(b) With reduced flow rate, but keeping the same salinity and temperature

(c) Electrolyte flow blocked after initial filling

(d) With low saline electrolyte, keeping flow rate and temperature unaltered

(e) Flow rate was normal but the effective surface area of the active plates got reduced.

(f) Stored electrolyte (solid) with fresh water and re-circulated water mixture flowing through the battery.

2. EXPERIMENTAL PROCEDURE

Mg-AgCl battery developed consisted of magnesium alloy anode of AP-65 composition, which contained aluminium, zinc and lead along with magnesium in the composition range of aluminium 6.0 per cent to 6.7 per cent, zinc 0.4 per cent to 1.5 per cent, lead 4.4 per cent to 5.0 per cent, manganese 0.15 per cent to 0.30 per cent and the rest was magnesium. The cathode sheet was made up of pure *AgCl* material. Spherical glass beads were used as separators, while silver foil was used as current collector. The battery was assembled in a pile-type configuration. On either side of the pile, two end plates were fitted, one acting as positive end plate and the other as negative end plate.

The fully assembled battery consisted of large number of cells connected in series, in pile configuration. However, for carrying out laboratory tests scaled down modules were used. Each module consisted of a 10-cell having ten positive plates and ten negative plates connected in series, the plate size and assembly process being unaltered. The 10-cell module was then fixed in a non-metallic holder which had a provision for inletting the electrolyte from the bottom and exit from the top. It was then fitted in the test rig system, connecting the two terminals of the battery to the fixed-resistance load.

Synthetic seawater of required salinity was prepared using de-ionised water, $NaCl$ and $Mg_2SO_4.3H_2O$ of LR grade. The actual salt content of the electrolyte was measured by drying a fixed volume of solution and weighing the solid material. The electrolyte was then cooled in a chilling unit to a required temperature. The electrolyte outlet tube of the 10-cell module, assembled in the test rig system, was connected to a 10 mm height of column to maintain 1 kg/cm^2 pressure at the battery outlet. The test rig system has been designed to provide fixed flow of electrolyte into the battery as per the requirement, measured using the online flow meter.

The 10-cell battery was discharged against a load bank with a calibrated resistance of 0.60 Ω and 200 A capacity. In actual usage, the battery was required to be discharged for 6 min. However, in the present 10-cell module tests, the discharge was continued beyond 6 min and data collected. The parameters recorded, during the discharge of the 10-cell modules were:

(a) Battery output voltage was recorded initially at 10 samples per second for 30 s to find the activation time and later at a rate of 1 sample for every 5 s up to the end of discharge.

(b) Battery discharge current was recorded initially at 4 samples per second for 30 s and later at 1 sample for every 5 s up to the end of the discharge.

(c) Static pressure head, every 30 s

(d) Electrolyte inlet flow rate, every 30 s

(e) Electrolyte inlet temperature, every 30 s

(f) Electrolyte outlet temperature, every 30 s

3. PERFORMANCE DETAILS

The results of various experiments conducted on the 10-cell modules of the battery, simulating different failure mode conditions have been discussed. However, the first experiment describes the test conducted and the results obtained during discharge of 10-cell battery under normal conditions of electrolyte salinity, temperature and flow rate. These results have been taken as reference for the failure modes studied subsequently.

3.1 Normal Electrolyte Flow Condition

The electrolyte flow parameters were fixed based on the actual requirements of the battery. Accordingly, the following were the conditions under which the 10-cell module was discharged:

(a) Electrolyte flow rate : 2.3 lpm

(b) Electrolyte salinity : 3.36 per cent

(c) Electrolyte conductivity : 37 m mho cm at 20 °C

(d) Inlet electrolyte temperature : 20 °C

The 10-cell module along with the holder was fitted into the test rig system connecting the electrolyte ports and the load resistance. The battery got activated the moment electrolyte flows through the battery. The discharge was continued

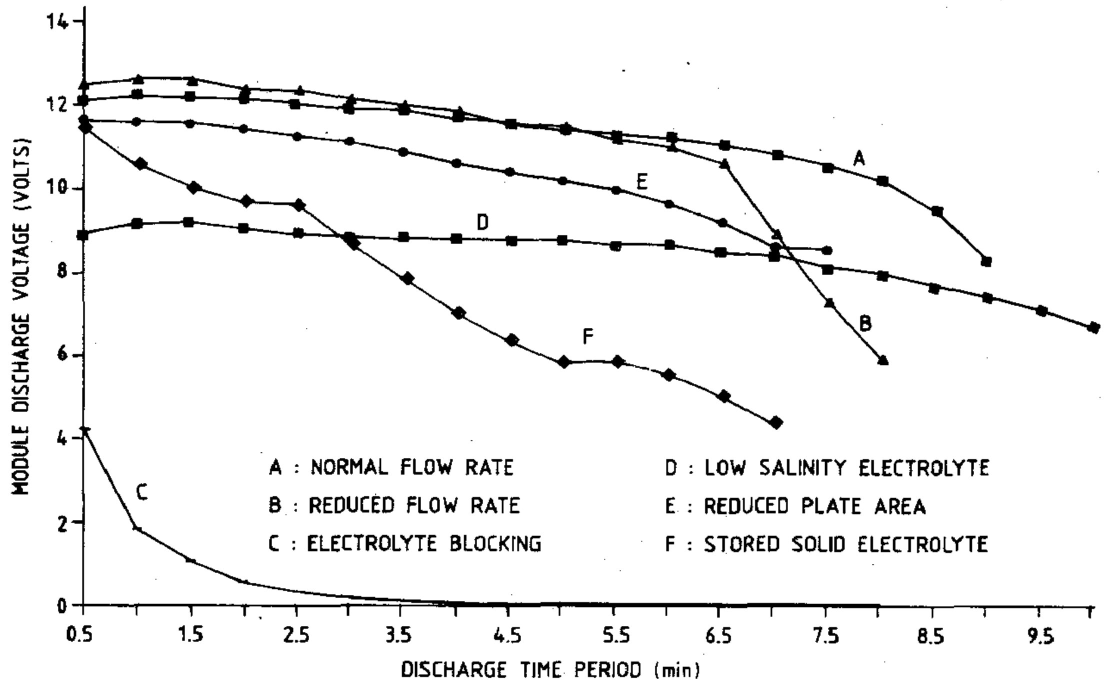

Figure 1. On-load voltages of different 10-cell modules under different conditions

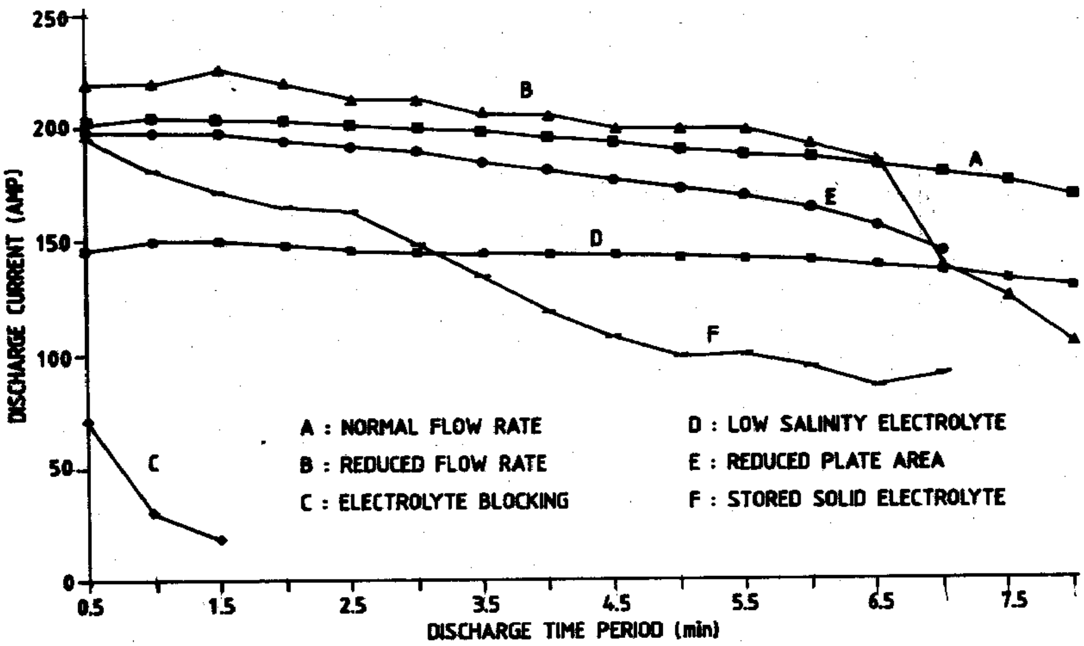

Figure 2. Discharge current behaviour of 10-cell modules under different discharge conditions

for 9 min. The discharge voltage of the 10-cell module is shown in Fig. 1. It can be seen from the figure that the voltage falls gradually from the initial maximum of 12.24 V to 11.19 V at the end of 6 min. As the battery was subjected to very high discharge rates (10 °C), the discharge curve is not expected to be flat. In addition, the water- activated batteries in general have the typical characteristic of continuous fall in voltage. The discharge current of the battery, as shown in Fig. 2, exhibits similar

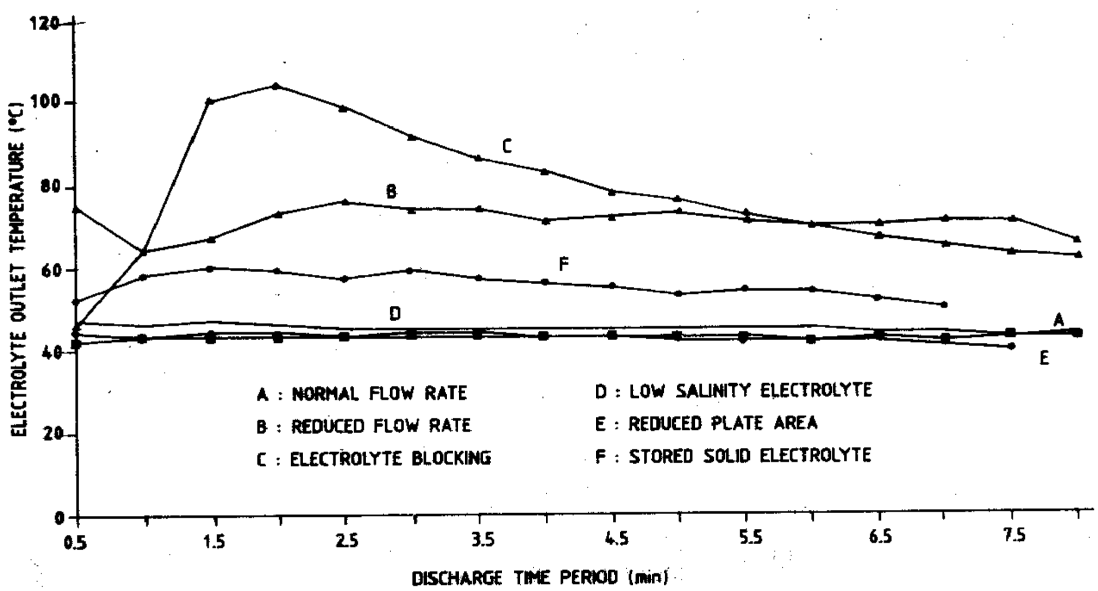

Figure 3. Electrolyte outlet temperature variation during discharge of 10-cell modules under different discharge conditions

Table 1. Discharge performance of 10-cell modules under different test conditions

Parameters	Test A	Test B	Test C	Test D	Test E	Test F
Max. Voltage (V)	12.24	12.66	12.040	9.210	11.66	12.12
Min. Voltage (V)	11.19	11.00	0.035	8.660	9.66	5.53
Avg. Voltage (V)	11.82	11.83	6.030	8.935	10.66	7.41
Max. Current (A)	204.70	226.00	200.700	150.600	199.00	196.0
Min. Current (A)	187.20	193.00	18.000	142.000	164.66	94.67
Avg. Current (A)	197.50	209.50	109.400	145.700	181.83	140.2
Max. Power (kW)	2.51	2.86	2.420	1.390	2.32	2.38
Min. Power (kW)	2.09	2.12	0.0006	1.230	1.59	0.52
Avg. Power (kW)	2.33	2.48	0.660	1.300	1.94	1.04

behaviour. The initial maximum observed was 204.7 A, which had fallen to 187.2 A at the end of 6 min. The average on load voltage during 6-min of discharge was 11.82 V and the average current 197.5 A, resulting in an average power output of 2.33 kW. These results are shown in Table 1.

The electrolyte outlet temperature recorded during discharge was 43 °C as shown in Fig. 3, which has remained almost constant during the entire period of discharge. The static pressure buildup was up to 1.1 kg/cm^2 at the electrolyte inlet point, which also remained constant during discharge. The battery activation time (the time taken by the battery to reach a fixed value of voltage from the moment of electrolyte entry into it) is very critical for the underwater vehicle operation was also recorded for the 10-cell battery.

The minimum voltage value required to be recorded before 4 s (which is the maximum time allowed) was fixed at 7.0 V. This activation curve shown in Fig. 4 indicates that it has 2.5 s for the battery to reach the specified minimum voltage, which is within the acceptance range. The total power generated by the battery during 6 min of discharge has been plotted in Fig. 5.

The external load was disconnected from the battery, once there was a steep fall in on-load voltage and discharge current. However, the flow of water through the battery was continued for some more time till the battery was cooled by which time it is considered that most of the magnesium anode was consumed. Later, the 10-cell module assembly was removed from the test rig system.

3.2 Electrolyte Low Flow Condition

As the performance of the battery is dependent on the electrolyte flow conditions, it is essential to maintain required electrolyte flow through the battery within narrow acceptable limits. However, during the vehicle operating conditions, there could possibly be a situation, where the flow of seawater into the battery is affected. This can happen due to many reasons, which include:

(a) Incomplete opening of scoop (which allows the seawater to flow through the battery)

(b) While launching the vehicle into the sea

(c) Obstruction in the electrolyte flow path inside the battery compartment, either at inlet or at the outlet, by some solid materials or objects.

(d) Resistance to the electrolyte flow through the battery plates due to clogging of reaction products formed during battery discharge.

To study the effect of low flow rate of the electrolyte into the battery, as against the normal flow rate, on the electrical performance of the battery and other related parameters, one 10-cell module is discharged at low flow rate. The flow rate fixed in the present experiment was approximately half of the normal flow, namely, 1 lpm. Electrolyte salinity and inlet electrolyte temperature were kept same as for the first experiment, i.e., 3.36 per cent and 20 °C, respectively. The static pressure head of 1.0 kg/cm^2 was kept at the electrolyte outlet point.

The on-load voltage of the battery is shown in Fig. 1(b). It can be seen from the discharge voltage curve that there is an increase in the voltage values [Fig. 1(b)] compared to the normal value [Fig. 1(a)] for the first 4 min. This is expected as the electrical performance of the battery is inversely proportional to the electrolyte flow rate. Also, it can be seen from the above plot that the voltage falls steeply after 6 min of discharge, while for normal flow battery it remained steady even up to 8 min of discharge. The discharge current values also show similar trend. Though the initial current maximum exhibited was 226 A, the value had fallen to 106 A after 8 min of discharge. It can also be noted from these curves that the rate of fall of voltage/current is more, compared to the normal curves. The battery output power plotted in Fig. 5(b) exhibits cumulative characteristics of voltage and current.

The other parameters recorded during discharge indicated that the electrolyte outlet temperature had exhibited a maximum of 76 °C which fell down to 68 °C at the end of 8 min. The electrolyte outlet temperature has been plotted [Fig. 3(b)]. It can be seen from the plots that battery with low flow rate exhibited higher electrolyte outlet temperature throughout the discharge, as expected. As can be seen from Fig. 4(b), the activation time too has got delayed as compared to the normal battery (curve A). All these values are shown in Table 1.

3.3 Electrolyte Blocked Condition

Another failure mode considered was the situation where the electrolyte filled the battery with a normal flow rate initially. However, after filling the battery, the electrolyte got blocked and there was no further flow of electrolyte into the battery. This possibility considered is based on the assumption that while the initial phase of the underwater vehicle run is normal, in the latter phase during the course of the run, the battery gets choked or either electrolyte inlet or outlet is blocked, thereby leading to no-flow condition. The purpose was to know the kind of behaviour the battery was going to exhibit in such situation, and what effect the vehicle would have. An experiment was conducted simulating these conditions and discharging one 10-cell module.

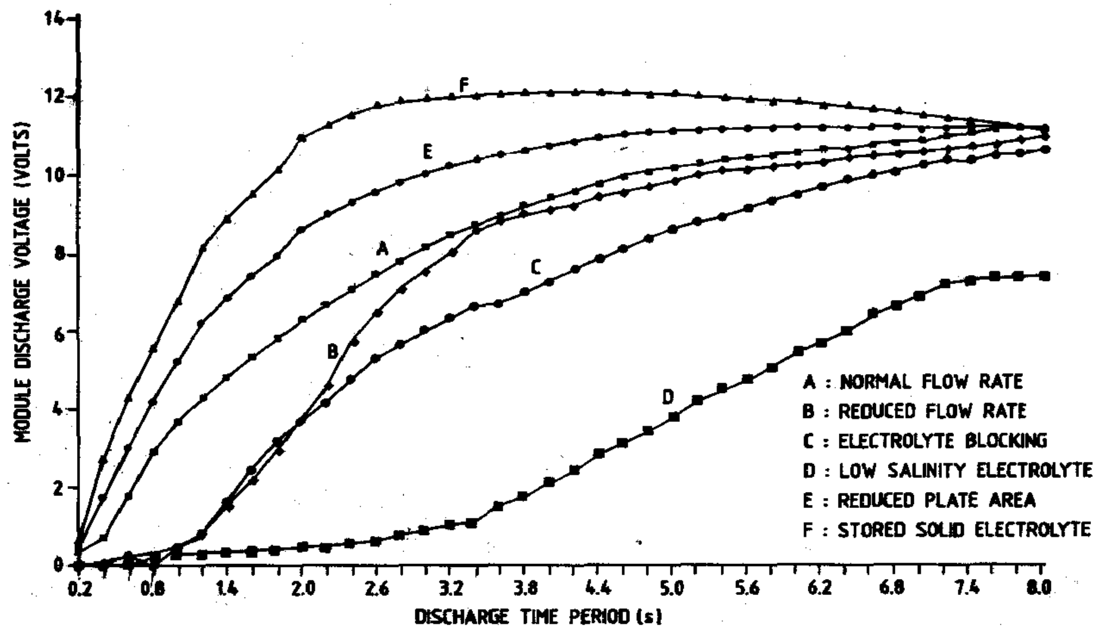

Figure 4. Activation curves of different 10-cell modules under different discharge conditions

The discharge voltage characteristics of the battery is shown in Fig. 1(c). It can be seen that the initial normal on-load voltage value drops almost to zero immediately after stoppage of the electrolyte flow. Similar observations of discharge current can be seen from the plot of Fig. 2(c). The interesting observation made in this discharge study is the battery outlet electrolyte temperature as shown in Fig. 3(c). There is a sharp increase in temperature within a minute of electrolyte flow stoppage, reaching the boiling point of the electrolyte. The battery remained hot for quite some time. This indicates that the electrolyte remained in the battery between the plates is used up in the corrosion reaction, in which magnesium alloy anode reacted with the electrolyte generating heat with the consumption of available electrolyte. This corrosion reaction, which appears to be a vigorous reaction, caused electrolyte depletion and subsequent voltage and current fall. These observations indicate that due to any reason if the electrolyte inlet or outlet paths are blocked or choked during the operation of the underwater vehicle, within a short time there will be steep fall in battery output power. However, the possibility of the trapped electrolyte boiling out of battery compartment may not occur in real situation, due to free availability of seawater at both ends of the battery.

3.4 Low Salinity Electrolyte

This underwater vehicle is tested exclusively in sea because of the requirement of saline water for proper functioning of the propulsion battery. However, the salinity of sea water is not same everywhere. This variation in the salinity of electrolyte alters the performance of the battery, and consequently the performance of the vehicle. It is known that the performance of the battery decreases with a decrease in the salinity of the sea water. However, to know exactly the reduction in the power output from the battery, it is felt necessary to carry out one 10-cell battery discharge study with decreased salinity of synthetic sea water. Water salinity of a natural lake which has required length, width and depth and facilities for testing underwater vehicle performance studies is taken as a reference in the present discharge study. Salinity of this lake water was estimated as 0.45 per cent which is about $1/7^{th}$ of the seawater salinity having a conductivity of 8 m mho-cm at room temperature. Synthetic seawater of above salinity was prepared and its conductivity checked so as to match with the requirement. The battery was discharged at 27 °C of electrolyte inlet temperature with a normal flow rate of 2.3 lpm.

The results have indicated that the discharge performance of the battery is strongly dependent on the salinity of the electrolyte. The on-load voltage delivered by the battery as shown in Fig.1(d) was between 9.2 V and 8.7 V for 6 min. However, the curve was very flat and discharge could be continued for longer periods. Similar performance was observed for discharge current as shown in Fig. 2(d). The electrolyte outlet temperature recorded was also relatively less (39 °C), as indicated in the curve D of Fig. 3. As expected, the average power output of the battery was low, (1.295 kW) for 6 min of discharge, almost half the normal value. This flatness of discharge voltage is considered to be due to relatively lower discharge current density of the battery plate and also possible removal of sludge and gas (lesser in quantity) more effectively. The lower discharge voltage could be due to low salinity and lesser electrolyte temperature.

There is a considerable delay in the activation time as can be seen from Fig. 4(d). It has taken about 7 s to reach the minimum voltage of 7 V, which is more than twice compared to the normal performance. This high value of activation time is not acceptable for the vehicle operation. However, due to draw of low currents, the discharge process was sustained up to about 10 min.

3.5 With Reduced Plate Area

Another probable failure mode considered is the situation where the electrolyte does not come into contact with full surface area of the plates. This reduction in active surface area could arise either due to electrolyte flow pattern and vehicle position or due to the products blocking part of

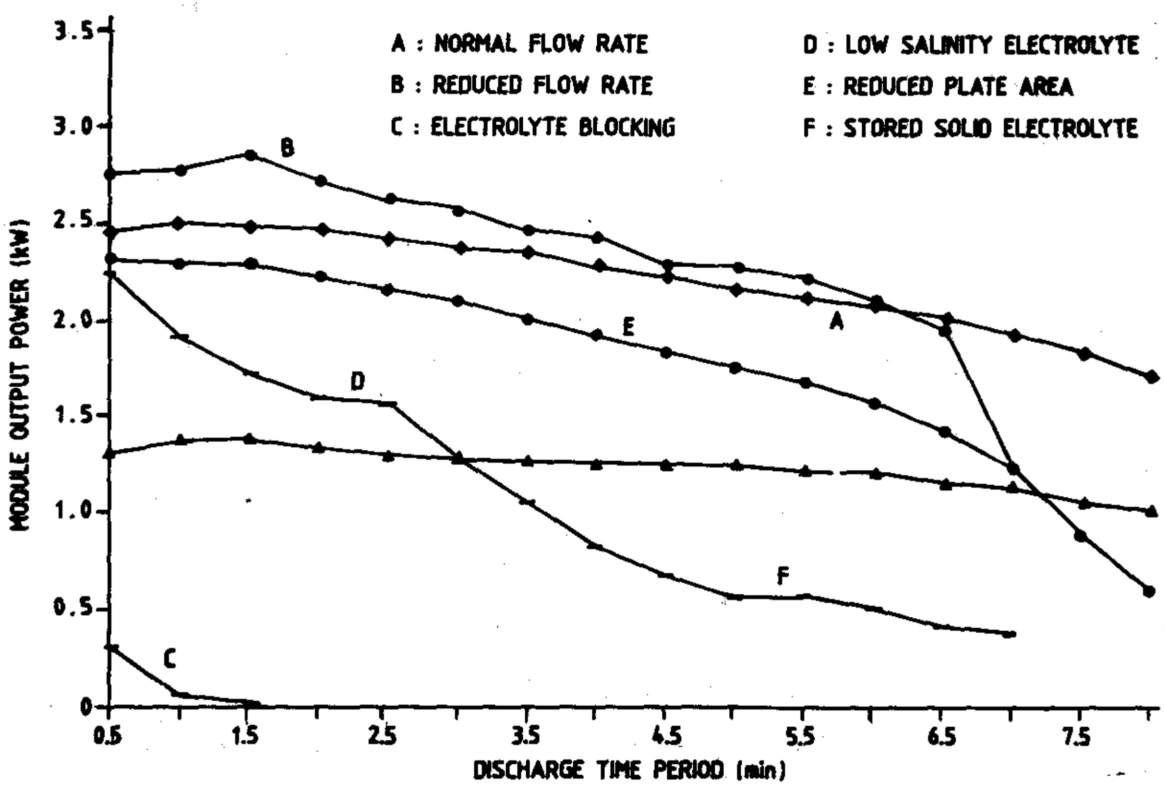

Figure 5. 10-cell modules output power variations under different test conditions

the active material surface. Testing a battery with reduced electrode surface is expected to result in an increased discharge current density, because the discharge current will try to remain unaltered for a given on-load voltage. This affects the on-load voltage of the battery reducing it from the normal value which in-turn reduces the discharge current. The final outcome would be a reduced power output from the battery, resulting in vehicle speed reduction. It was felt necessary to study the effect of reduction of battery plate area, on its discharge performance experimentally, by carrying out a 10-cell load test. For carrying out this experiment, during the assembly of 10-cell module, the geometric area of the cathode sheet was reduced by 12 per cent at the top of the plate. The other beneficial effects expected to accrue from this were: (i) reduction in the weight of the battery by about 10 per cent and (ii) increase in the metacentric height, due to lowering of CG level, resulting into more stability to the vehicle.

The discharge of 10-cell module was carried out under normal electrolyte flow conditions, normal salinity and temperature of the electrolyte. The results obtained were plotted and shown in the respective figures. As can be seen from the discharge voltage curve E of Fig. 1, the on-load voltage of the battery starts from a maximum of voltage of 11.66 V and falls to 9.66 V by the end of 6 min. Both these values are low compared to the normal discharge values. Similarly, the load current as shown in Fig. 2(e) was also less, varying between 199 A to 165 A. As expected, the power output from the battery too was less.

The temperature of the outlet electrolyte is shown in Fig. 3(e). Even this value was also low compared to the normal value due to decreased current. The important observation from this discharge data was that not only the battery output voltage was low, the rate of fall of voltage with time was also more, resulting into rapid fall of battery output power with time. The recordings which were made up to 7.5 min indicated that the performance of the battery deteriorated fast with time, unlike the normal battery. However, the activation time was not affected, as indicated in Fig. 4(e). The effect of decreased battery output voltage and current was reflected in the total output power of the battery, as shown in Fig. 5(e).

3.6 With Stored Solid Electrolyte

The *Mg-AgCl* reserve pile battery works almost exclusively with seawater. The salt content of the seawater acts as electrolyte for the battery. Though there are many advantages of using such a battery for underwater propulsion purpose, there are some disadvantages also. The major disadvantage is that this battery restricts its use in seawater/saline water and fails to perform satisfactorily in fresh water. This restricts the usage of the vehicle in seawater only. To study the possibility of overcoming this limitation, it has been planned to store solid electrolyte and discharge the battery with a mixture of fresh water and recirculated water. In this condition, the fresh water first mixes with the solid electrolyte and carries it through the battery plates, thereby making the battery to operate normally. However, after 30 s, the fresh water is mixed with recirculated water which comes out of the battery at a rate of 1.8 lpm and 0.5 lpm, respectively. The positioning of the solid electrolyte in the electrolyte flow path, the content of the solid electrolyte and the form in which it is to be stored and contained has been studied in detail. Different 10-cell modules were assembled by verying the above parameters and discharge tests have been conducted. The discharge characteristics of the best performed battery are described here.

The solid electrolyte mixture consisting of $NaCl$ and $MgSO_4$ in the specified ratio was mixed and kept in a non-woven polyamide bag. The aim was to dissolve the salt gradually during passage of fresh water through it, so that the required salinity was maintained throughout the discharge. The placement of salt bag creates two problems: first, there is no sufficient space to place it inside the battery, and second it is going to increase the weight of the battery. Hence, to meet both these requirements, the $AgCl$ positive plate was cut at the bottom to reduce the geometric area from 570 cm^2 to 470 cm^2. The weight reduction was 285 g for the 10-cell module. The empty space created by reducing the plate area is not sufficient for keeping equivalent amount of solid electrolyte, because of the density difference between $AgCl$ and the solid electrolyte. An electrolyte salt bag containing 160 g of the salt could be placed. The discharge of the module was carried out with normal flow conditions of 36 °C inlet temperature of fresh water with a flow rate of 2.3 lpm. The results obtained are shown in the figures.

From the curve F of Fig.1, it can be seen that the maximum voltage reached in the initial stage was 12.12 V which had occurred at 4.1 s. However, this voltage had fallen rapidly, reaching to 5.53 V by the end of 6 min of discharge. There was a continuous fall of voltage from the beginning; however, a small plateau was observed up to 2.5 min. Thereafter, the fall of voltage was more steep. The corresponding discharge current had also exhibited similar trend, falling to 95 A from 196 A by the end of 6 min, as can be observed from the curve F of Fig. 2. The variation in the electrolyte outlet temperature with time, during 6 min of discharge is shown in Fig. 3(e). Though the temperature has reached ~ 60 °C, it had fallen to 54 °C by the end of 6 min. The activation curve recorded is shown in Fig. 4(f). The performance of the battery though looked satisfactorily in the initial period of 3 min deteriorated very fast thereafter.

4. RESULTS & DISCUSSION

The results obtained from the discharge studies of various 10-cell modules carried out under different conditions, have been shown in Table 1. It can be seen that the power output for the normal battery varies from 2.51 kW to 2.09 kW during 6 min of discharge, with an average of 2.33 kW. This means the power variation from the battery to the propulsion motor is within 10 per cent. As the speed is cube related to the power output, it can be considered that the vehicle speed will vary marginally during 6 min of operation, which may be acceptable. The activation time is within the acceptable range. The electrolyte temperature has increased by 23 °C, which has remained constant throughout discharge.

However, during the second test in which the flow rate of electrolyte into the battery was reduced to half, as expected, there was an improvement in the average output of the battery. However, the rate of fall was more severe, reaching 2.12 kW from 2.86 kW in 6 min. It means that the vehicle will have an initial high speed which falls off steeply with time. This has been considered a disadvantage from the vehicle performance point. Also as the power delivered is more in the initial phase, the rate of fall is more prominent in the latter phase, causing a steep fall in the final phases. From the results of the third test in which the flow rate was intentionally stopped after filling of battery, it was clear that stoppage of flow under any circumstances would result into vehicle's premature run termination. However, electrolyte starvation may not take place as long as the vehicle is in contact with seawater.

With reduced plate area, there was an overall reduction in the battery output power. Additionally, it was noticed that the rate of fall was also more than the normal, varying from 2.32 kW to 1.59 kW in 6 min. The results indicated that though the reduced plate area was not detrimental to the vehicle operation, it was not preferred, because of the above-said reason.

The discharge tests conducted under low salinity electrolyte and using solid electrolyte inside the battery were meant to study the possible use of the vehicle in fresh water or near-fresh water lakes. It was observed that testing the battery at low salinity resulted into drastic reduction in battery output power to unacceptable levels. It could also be noted that the battery activation time got delayed to dangerous levels, detrimental to the vehicle. However, as the power levels were low, the output power was flat and discharge continued for long periods. Storing solid electrolyte into battery does not help in improving the performance of the battery in anyway. These results indicated that the underwater vehicle using *Mg-AgCl* battery operated satisfactorily in seawater only.

5. CONCLUSIONS

For design, development and proving of any system, it is essential that each sub-system is required to be studied in detail. Identification of various possible failure modes and study and evaluation of performance of each sub-system under these conditions is a necessity. The results of various experiments conducted on the performance of the propulsion battery under different failure mode conditions will help in understanding the conditions for proper performance of the underwater vehicle along with vehicle mission failure conditions wrt propulsion battery.

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