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Basic Of Electric Energy Storage

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Project Report
Analysis of a GreenRock battery

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Development of a model for a lithium ion cell

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1. What are saltwater batteries?

"The increasing interest in energy storage for the grid can be attributed to multiple factors, including the capital costs of managing peak demands, the investments needed for grid reliability, and the integration of renewable energy sources. Although existing energy storage is dominated by pumped hydroelectric, there is the recognition that battery systems can offer a number of high-value opportunities, provided that lower costs can be obtained." [5]

Over the last decades Lithium-ion batteries in particular have enabled major progress in the use of portable devices and thus raised the standard of living globally. However, due to the further development and increasing decentralization of electricity production, new solutions are needed for the short-term intermediate storage of electricity. However, there are doubts that lithium-ion batteries are the key to a smart grid, as the raw materials needed for production are both scarce and expensive.

For this reason, intensive research is being carried out into other battery technologies, with saline water batteries standing out as stationary energy storage systems. The main arguments for the use of sodium-ion batteries are thus, on the one hand, the cheap raw materials available in large quantities. On the other hand, sodium-ion batteries behave chemically very similar to lithium-ion batteries, which makes saltwater batteries an interesting alternative. [4]

The development of new construction materials, such as metal oxides as cathode or carbon as anode material, is particularly interesting. The GREENROCK battery presented below also uses these novel materials. Apart from the conductive components, however, there is also further potential for development regarding the design of the individual cell or the expansion of the application range of saltwater batteries. [4] In a 2013 published study M. Saiful Islam and Craig Fisher conclude: "(…) whichever direction the future takes, it is clear that major advances in lithium- and sodium-ion batteries for electronics, electric vehicles and grid storage will depend on exploring new materials and concepts, and on a greater fundamental understanding of their operation on the atomic and nano scales. "[6]

Saltwater batteries have been researched since the 1970s and have been used successfully in practice in recent years. However, they do not yet play a major role on the battery market compared to the market-dominating lithium-ion technology. The term sodium-ion accumulator describes all battery technologies with sodium ions, such as sodium nickel chloride batteries. However, these belong to the group of thermal batteries and differ from the GREENROCK saltwater battery considered below in their operating temperature of 250 - 350°C. In addition, redox-flow batteries with sodium ions can also be counted among the sodium accumulators, but these differ from GREENROCK stacks. The redox-flow battery is based on two energy-storing electrolytes which circulate in two separate circuits, while the GREENROCK stack uses only one electrolyte which does not circulated. [2]

The GREENROCK Stack Saltwater Battery is a sodium-ion accumulator model by the Austrian company BlueSky-Energy. This battery uses an aqueous sodium-ion electrolyte, which ensures that the battery is both non-toxic, deep discharge resistant, but at the same time neither flammable nor combustible. Another great argument for saltwater batteries is, that end-of-discharge voltages as low as 0V can be achieved, while not taking any damages over a longer period of time. In addition, the battery is maintenance-free and uses commonly found raw materials and operates in a temperature range of +5°C to +50°C. The disadvantages of saltwater batteries are their low energy density of 12 to 24 Wh/l and their low cycle stability. In addition, the capacity of the battery is strongly dependent on the discharge current, which makes the saltwater battery unsuitable for mobile applications. [1,2,3,4]

Salzwasser Batterien werden bereits seit den 70er Jahren erforscht und in den letzten Jahren erfolgreich in der Praxis eingesetzt. Jedoch spielen Sie im Vergleich zur marktbeherrschenden Lithium-Ion Technologie noch keine große Rolle. Der Begriff Natrium-Ionen-Akkumulator beschreibt weiter gefasst alle Batterietechnologien mit Natrium-Ionen, wie beispielsweise Natrium-Nickelchlorid-Batterien. Diese gehören jedoch zu den Thermalbatterien und unterscheiden sich mit ihrer Betriebstemperatur von 250 – 350°C von der nachfolgend betrachteten GREENROCK-Salzwasser Batterie. Zusätzlich können auch Redox-Flow Batterien mit Natrium-Ionen zu den Natrium-Akkumulatoren gezählt werden, jedoch unterscheiden diese sich von GREENROCK Stacks, da die Redox-Flow Batterie auf zwei energiespeichernden Elektrolyten basieren, welche in zwei getrennten Kreisläufen zirkulieren.

The GREENROCK Stacks battery is designated for stationary applications like for ordinary housing, commercial energy storage units and island solutions and the whole system can be sized up modularly up to 30 kWh. [1]

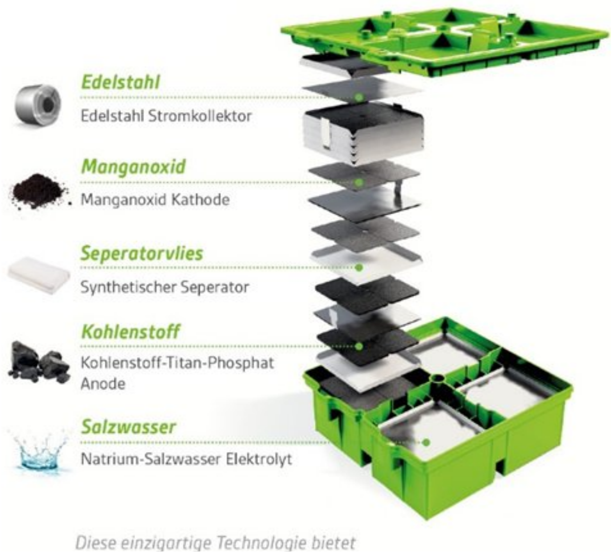


Figure 1: The structure of the GREENROCK Stacks battery (https://www.bluesky-energy.eu/wp-content/uploads/2020/03/Aufbau-Baterie.jpg, zuletzt geprüft am 10.06.2021)

In Figure 1 the batteries structure is presented. The battery consists of current collectors made of stainless steel, which lie on a cathode made of mangan oxide. A synthetic fleece serves as a separator, which separates the cathode from an anode made of carbon-titanium-phosphate. A solution of sodium saltwater serves as the electrolyte. Each stack consists of eight layers, each consisting of four cells. [1]

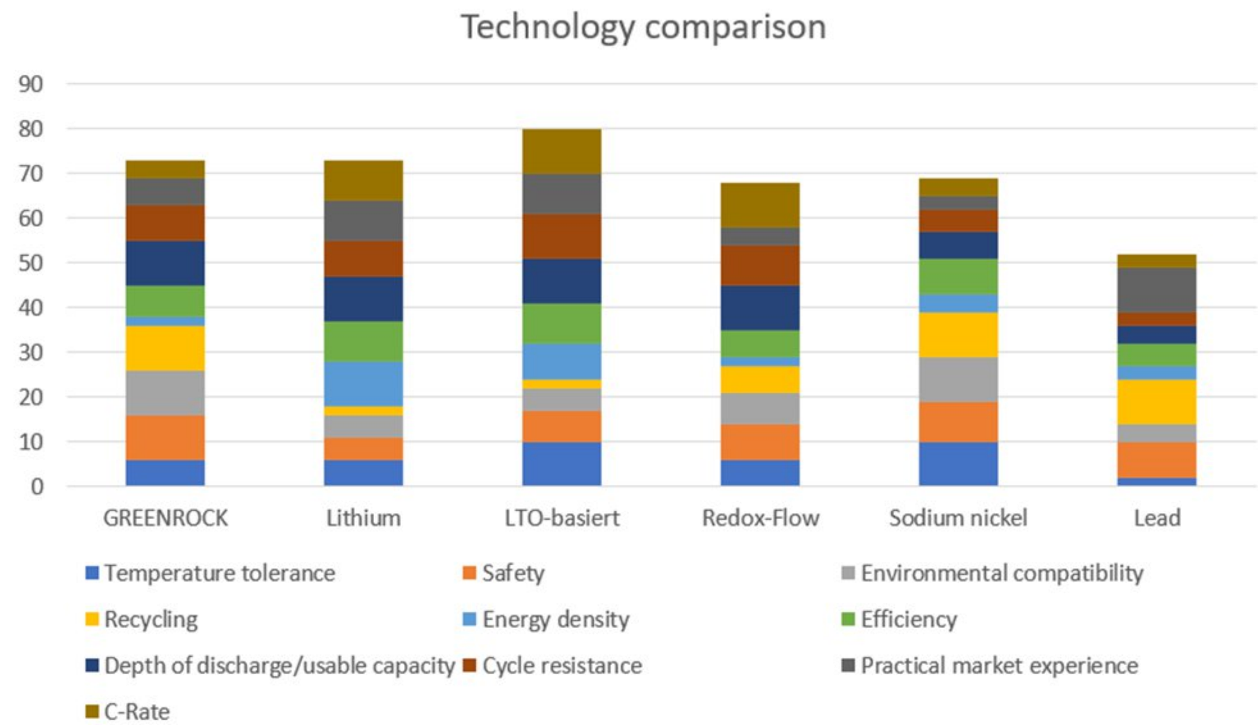


Figure 2: A comparison of the available battery technologies (https://www.bluesky-energy.eu/wp-content/uploads/2021/05/technologycomparisation.png, zuletzt geprüft am 10.06.2021)

Figure 1 compares the saltwater technology of the GREENROCK Stacks model with competing battery technologies. It is striking that the energy density and C-rate of the saltwater battery clearly lag behind the competing technologies. However, this is compensated by the remarkably high safety and the particularly large depth of discharge. Another great feature is the above average recyclability of GREENROCK's battery. This makes the saltwater battery by GREENROCK a strong alternative to widely used Lithium-Ion batteries, for now at least in stationary applications. [2]

3. Battery parameter identification

The aim is to gain as much information as possible by only monitoring the current and voltage behavior of a battery without being able to look inside.

To determine the individual model parameters, the battery is excited with different load profiles and the current-voltage behavior is then compared between simulation and measurement. Successive parameter variation is used to determine the parameter set that leads to the best agreement under the given conditions. This procedure of aligning measurement and simulation is also referred to as fitting in the following. It is possible to obtain the parameter set in both frequency and time domain by fitting. An efficient simulation of the model behavior is absolutely necessary for this parameter fitting.

Of course, not all parameters can be determined in this way at the same time. On the one hand, the computational effort would be too great with so many degrees of freedom, and on the other hand, the simultaneous variation of a large number of parameters carries the risk that the fitting algorithm will identify a suboptimal parameter set that is too far removed from reality. [cf. 1]

The challenge is to develop load scenarios that only deflect individual or a few processes inside the battery so that these can be recorded in isolation. If a certain number of parameters is considered to be certain, this knowledge can considerably facilitate the parameterization of the remaining parameters. [cf. 2]

A very important influencing factor here, for example, is the dynamics. If the battery is excited with a high frequency alternating current, the processes with slow dynamics do not take place at all. Another influencing factor is the variation of state of charge or temperature. In the measurements, individual processes can be masked out if they have no influence on the battery voltage at a certain state of charge, or individual processes that are dominant at high or low temperatures can be considered in isolation.

The amplitude of the deflection can also be used to distinguish individual processes. For example, small-signal excitation should have no effect on the volume ratio of two coexisting phases of different concentration in the active mass. Large-signal hysteresis behavior, if present, is not excited.

The parameterization of an actual in-situ model is so far not possible due to the voltage behavior alone. Even if the derivation of the individual model parts is based on physical principles, it must always be kept in mind that only a single process or particle can never be observed in the voltage behavior. Even if, for example, a region has been identified in the impedance spectrum that can be assigned to an intercalation reaction, the behavior assigned to the reaction is always influenced by the electrode geometry. For this reason, in the rarest of cases, an easily derivable curve will occur for the individual parameters as a function of temperature, state of charge or current intensity. [cf. 1]

As a consequence for the model parameterization, this means that all states for which the model is to be valid afterwards must also be captured at least approximately in the parameterization measurement. [cf. 2]

The measurement procedure is therefore designed in such a way that individual states are set in succession and at these points the parameterization measurements are carried out. The defined state must not be left during the measurement. After the evaluation a characteristic curve with different temperatures, states of charge and, depending on the model part, also currents are obtained for each parameter. The calculation of the behavior is done by tracking the relevant state variables and by interpolation between the grid points of the characteristic curves.

It is essential to avoid that the fitting algorithm converges to a local minimum of the optimization variable. However, the view into the battery, which is limited to the electrical measured variables, makes it difficult to evaluate the result. An important criterion for a valid parameter set is therefore a smooth and plausible curve over temperature and state of charge. The more grid points are recorded, the easier it is to check the plausibility of the generated parameter field. [cf. 1]

4. Measurements

In order to gather meaningful data while evaluating the performance of an electrical energy storage system, it is crucial to stick to certain standards in battery testing. The Institute of Electrical and

Electronics Engineers (IEEE) provides such standards in its document “IEEE Standard Test Procedures for Electric Energy Storage Equipment and Systems for Electric Power Systems Applications“.

4.1 General requirements

According to the above mentioned document certain general requirements have to be fulfilled when testing energy storage equipment and systems (ESS). The test environment conditions have to be kept in a reasonable range, the instruments used for testing need to be suitable and calibrated in time intervals and technical documents required to perform the tests should be provided by the manufacturer of the ESS. Furthermore the test executions and their results need to be precisely documented.

4.2 Different types of tests

In its standard the IEEE lists five different types of tests that should be performed on an ESS.

4.2.1 Type test

The type test is a series of measurements that aim to “verify the design principle and the design rating of the product“ [IEEE p.11] and analyse the condition of the ESS while performing its required functions. A full type test consists of 18 different tests including temperature stability test, state of charge test, and ramp-rate test (testing for maximum rate of power).

4.2.2 Production tests

Production tests are used to assess if the required quality and deviation is reached, and are performed before shipment of the ESS. The production test consists of nine different tests and includes continuous operation test, response to abnormal voltage conddition test, and overcurrent test.

4.2.3 Installation evaluation

After field installation of the ESS an installation evaluation shall be executed. Here the operation environment conditions, grounding, isolation device, monitoring and fault response are inspected and it is evaluated if they are in accordance with the applying IEEE standards.

4.2.4 Commissioning tests

Commissioning tests should be performed after the installation evaluation and before the beginning of actual operation of the ESS. Their aim is to “verify whether the technical indexes of ESS are in accordance with the operation requirements after delivery and installation“ [IEEE p.11]. The commissioning test consists of seven different steps including calibration and inspection, insulation test of paralleling equipments, synchronization and parameters adjustment.

4.2.5 Periodic tests

Periodic tests are performed in specified time intervals while the ESS is officially in application. The aim is to assess the safety and reliability while operating. A periodic test includes the following: SOC test, ramp-rate test, response to voltage abnormal test, etc.

Figure 1 shows the testing procedures suggested by the IEEE for a single piece of equipment and for a set of equipment units.

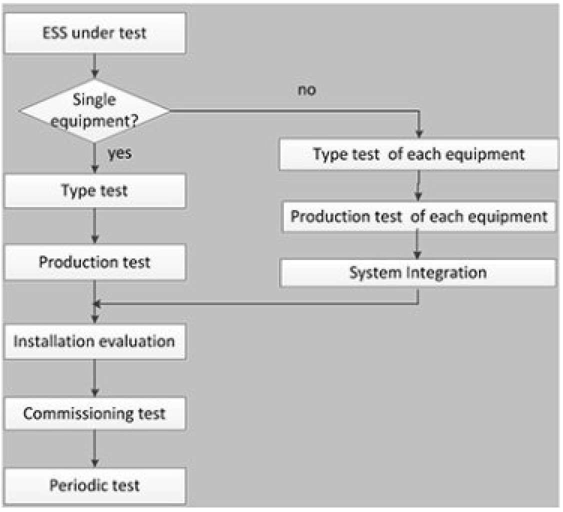


Figure 1: Testing procedures

4.3 Aim

Since the aim of the measurements in this case is not to fully verify the ESS but to lay a foundation for a simulation model, several measurements consisting of type tests, production tests, commissioning tests and periodic tests are out of scope. To set up a simulation model a pulse discharge sequence test is neccessary. The following pages will therefore focus on the measurements needed to build a simulation model of the saltwater battery covering the experimental setup and execution of the measurements as well as comparing their results to the actual simulation and the data sheet from the manufacturer.

4.4 Experimental setup

The equipment used for battery testing includes the Greenrock Battery stack with 48V, a 60A Neware battery testing system, power cables, measurement cables, a temperature sensor, two LAN cables, a network switch and a laptop that runs the required software for the battery testing system.
First the battery is connected to a battery testing system through power cables. Then the cables responsible for the measurements are connected to the battery and a temperature sensor is attached on its back using tape. This can be seen in Figures 2 and 3.

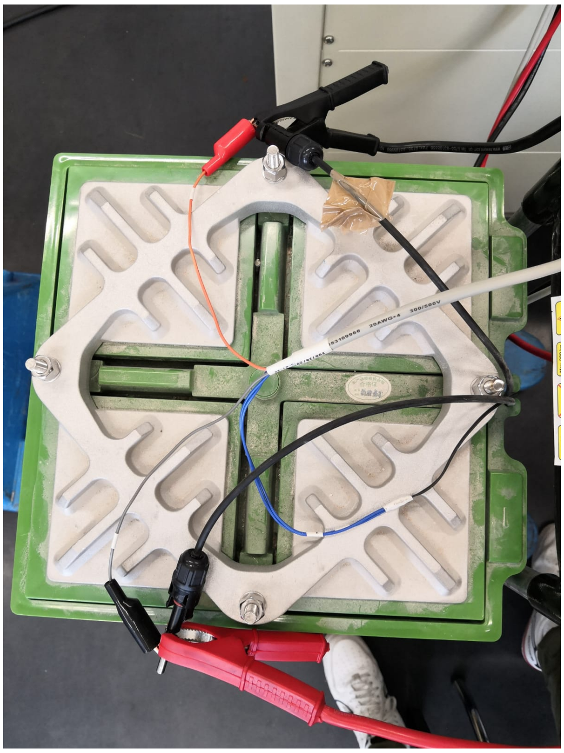


Figure 2: Connection to saltwater battery Figure 3: Attachement of temperature sensor

Furthermore the battery testing system needs to be connected to the network to enable remote access. This is done by using a LAN cable and plugging it into a free port on the same switch that the laptop is connected to. Once the laptop recognized the battery testing system can now be controlled in remote using TeamViewer to access the laptop in the laboratory. As seen in Figure 4 the laptop in the laboratory runs a testing software which is used to manage the battery testing system.

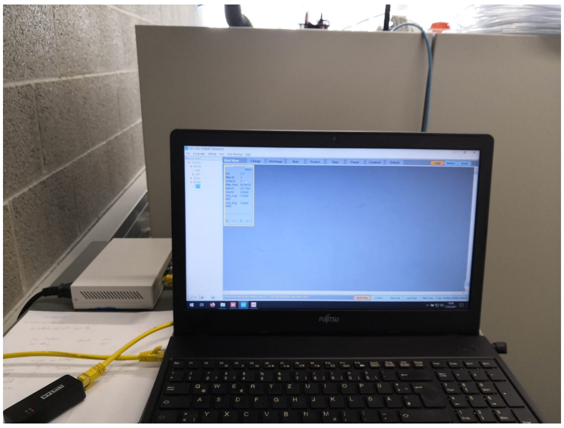


Figure 4: Laptop with battery testing software

4.5 Execution

The measurements are executed as follows. At the time of starting the measurements the battery has already adapted to room temperature and therefore does not need to rest much longer before starting the first step of the measurement. After resting for 10 seconds the battery is completely charged with constant current of 5A and constant voltage (CCCV) for 2 hours 26 minutes and 7 seconds. This is followed by a rest of 1 hour. Then the battery is fully discharged with constant current (CC) of 5A, after

that resting for 3 hours and getting charged with CCCV of 5A. After resting another 3 hours the cycle of measurements necessary for the simulation of the battery can be executed.
The cycle includes 4 different steps that shall be repeated 65 times. In the first step the battery is discharged with CC of 5A until a capacity of discharge of 2,2Ah is reached for that step.Then the battery rests for 45 minutes and is charged at CC of 5A until arriving at a capacity of charge of 0,2Ah. In the 4th step a rest of 15 minutes is wanted. Once all 4 steps are completed the cycle can start again at the first step. Due to a lack of time for battery testing caused by a limited availability of the batter stack the amount of cycles is reduced to 21. Figure 5 shows the steps that are executed including the fully charging and discharging of the battery to prepare for the pulse discharge sequence test.

Step	Task	Current	Capacity
1	Charge CCCV	5A	
2	Rest 1h		
3	Discharge CC	5A	
4	Rest 3h		
5	Charge CCCV	5A	
6	Rest 3h		
7	Discharge CC	5A	2,2Ah
8	Rest 0:45h		
9	Charge CC	5a	0,2Ah
10	Rest 0:15h		
11	Repeat Step 7-10 x21		

Figure 5: Test Matrix

5. Comparison simulation – reality – data sheet

Nowadays simulation is a common feature to make a prognosis about the expected yield and the operational behavior of batteries. In the following, the determined data from the simulation and the data from reality are compared with the data sheet.

Figure 1 presents the data obtained from the battery test. The last column shows the values for the capacity. Battery capacity [Ah] is defined as a product of the current that is drawn from the battery while the battery is able to supply the load until its voltage is dropped to lower than a certain value for each cell. The higher the discharge rate, the lower the capacity.

CyCle	Step	Raw Step ID	Status	Start Voltage(V)	End Voltage(V)	Start Current(A)	End Current(A)	CapaCity(Ah)
1	1	1	Rest	55, 6436	55, 6398	0, 0000	0, 0000	0, 0000
1	2	2	CCCV_Chg	56, 3281	58, 3072	0, 7874	0, 0000	3, 2048
1	3	3	Rest	58, 2961	56, 4174	0, 0000	0, 0000	0, 0000
1	4	4	CC_DChg	55, 6808	35, 0000	−0, 8184	−5, 0099	34, 1076
1	5	5	Rest	38, 5974	43, 5081	0, 0000	0, 0000	0, 0000
2	6	6	CCCV_Chg	44, 1406	57, 6078	0, 7285	0, 2480	37, 7366
2	7	7	Rest	57, 4069	56, 2611	0, 0000	0, 0000	0, 0000
2	8	8	CC_DChg	55, 1376	48, 6011	−1, 3640	−5, 0099	2, 2001
2	9	9	Rest	52, 5558	55, 0818	0, 0000	0, 0000	0, 0000
3	10	10	CC_Chg	55, 5505	59, 0215	0, 3131	5, 0037	0, 0001
3	11	11	Rest	55, 2046	55, 1302	0, 0000	0, 0000	0, 0000
3	12	8	CC_DChg	54, 4382	48, 8281	−0, 7936	−5, 0099	0, 3687

Figure 1: data from the battery test

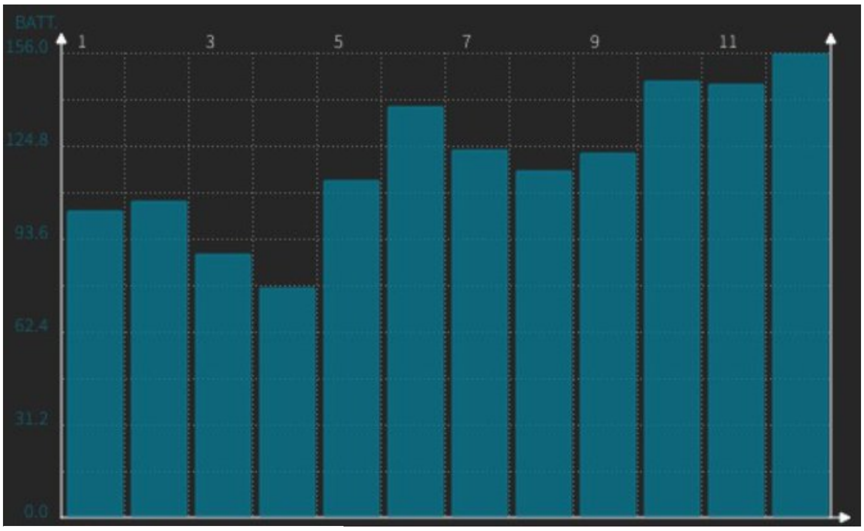
Figure 2 shows the capacity of charge [Ah] and capacity of discharge [Ah] as well as the cycle life [%]. The capacity that can be removed from the battery depends on the discharge method, i.e. the discharge current, the final discharge voltage of the battery (the voltage at which the discharge is terminated), and of course the state of charge. Various discharge methods are commonly used, including constant current discharge, constant resistance discharge, or constant power discharge. Depending on the discharge method, the battery has a different capacity. Therefore, in a meaningful specification of the nominal capacity, both the discharge current and the final discharge voltage must be specified. In general, the removable capacity of a battery decreases with increasing discharge current. The reason for this is both the increasing losses at the internal resistance of the accumulator and the fact that the chemical processes in the accumulator run at a limited speed.

Battery life has two meanings for rechargeable batteries. It can mean either the length of time a device can run on a fully charged battery or the number of charge/discharge cycles possible before the cells fail to operate satisfactorily. Available capacity of all batteries drops with decreasing temperature.

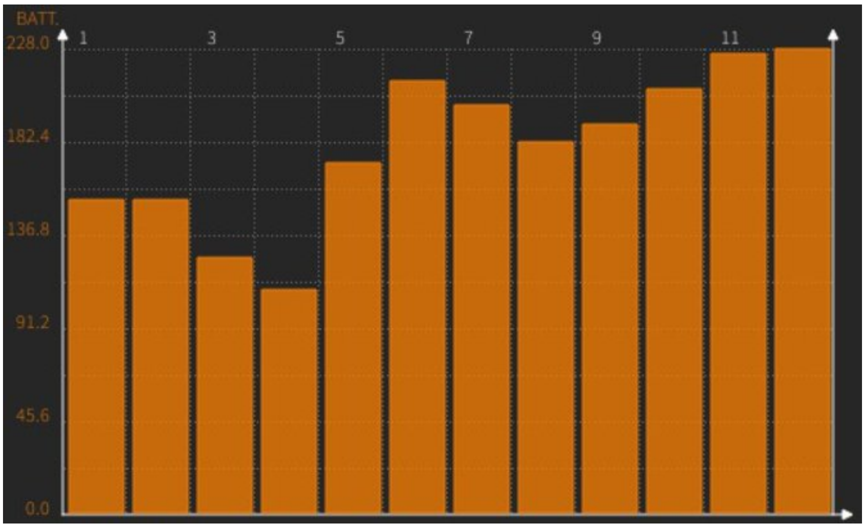
ToTal of Cycle	Capacity of charge(Ah)	Capacity of discharge(Ah)	Cycle Life(%)
1	3, 2048	34, 1076	100
2	37, 7366	2, 2001	6, 450524132
3	0, 0001	0, 3687	1, 080907481

Figure 2: capacity of charge, capacity of discharge, cycle life

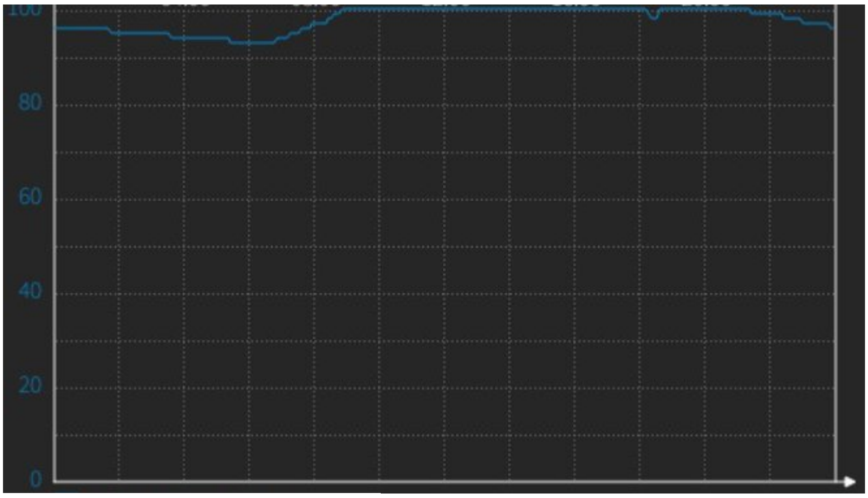
The three diagrams below show the battery discharge [kWh], battery charge [kWh] and state of charge [%] of a GREENROCK 48V saltwater battery in real life over a period of one year.



Battery discharge [kWh]



Battery charge [kWh]



Battery state of charge [%]

State of charge (SoC) is the level of charge of an electric battery relative to its capacity. The units of SoC are percentage points (0% = empty; 100% = full).

An alternative form of the same measure is the depth of discharge (DoD), the inverse of SoC (100% = empty; 0% = full). SoC is normally used when discussing the current state of a battery in use, while DoD is most often seen when discussing the lifetime of the battery after repeated use. According to the manufacturer, the depth of discharge of the saltwater battery tested here is 100% [cf. 1].

Finally, you can see the data sheet of the manufacturer, which contains values for the capacity [Ah], energy [Wh] and energy efficiency [%] of the 48V saltwater battery as a function of the charge current and discharge current.

Capacity (Ah)		Charge Current (A)		
		5A	10A	15A
Discharge Current (A)	5A	53.1	42.8	35.8
	10A	46.7	39.0	32.5
	15A	42.9	35.8	31.3

Energy (Wh)		Charge Current (A)		
		5A	10A	15A
Discharge Current (A)	5A	2565	2004	1619
	10A	2258	1827	1467
	15A	2071	1676	1414

Energy efficiency (%)		Charge Current (A)		
		5A	10A	15A
Discharge Current (A)	5A	88.5	87.6	86.2
	10A	85.0	84.2	82.0
	15A	83.8	82.0	80.0

Figure 3: data sheet [1]