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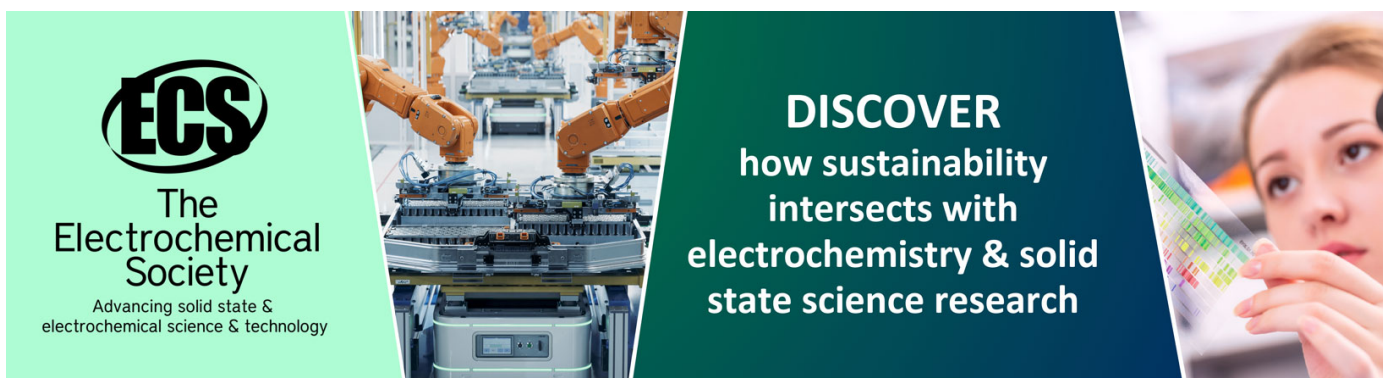
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Temperature Effects on Calendar Aging of Lithium-Ion and Nickel Metal Hydride Batteries

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Abstract. The effect of temperature on the calendar aging of commercially available 3.25 Ah Lithium-Ion (Li-Ion) and 2.30 Ah Nickel Metal Hydride (Ni-MH) batteries were investigated. Calendar life tests were carried out using open circuit method at -20°C, 20°C and 55°C temperatures and initial state of charge (100% SOC). It is found that the aging of the batteries increases with increasing temperature and storage time.

1. Introduction

Lithium-ion batteries are one of the most promising energy storage devices for many applications due to their high energy/power density and environmentally friendly characteristics such as portable electronic devices, electric vehicles and smart grid systems. In addition, long cell lifetime of lithium-ion batteries makes them advantageous than their competitors in most applications such as electric cars (up to 15 years). Lithium-ion batteries age with either charge/discharge cycling or storage duration. Most of the battery life is spent under storage in many applications. Therefore, the study of lithium-ion battery aging during storage seems particularly important. There are many studies on lithium-ion battery aging during storage in the literature [1-4]. Lithium-ion batteries experience reversible and irreversible capacity loss during storage. The reversible capacity loss also called self-discharge can be recovered by fully re-charging cell after storage. The irreversible capacity loss, namely aging of lithium-ion batteries over time, arises from many factors such as loss of active material, loss of cyclable lithium, increase in resistance that depend on storage conditions (temperature and voltage) and materials used for electrode and electrolyte [5-8]. (i) Loss of active materials originates from processes such as particle isolation, electrode delamination, material dissolution and structural degradation. (ii) Loss of cyclable lithium arises from side reactions that may take place at electrolyte/electrode interfaces (e.g., growth of passivation layers at both electrodes due to electrolyte decomposition). If the rate of lithium consumption at the negative electrode is different from the rate at the positive one, the cell experiences a loss of cyclable lithium due to an increase of the cell imbalance. (iii) Resistance increase of the cell results from passive films at the active particle surface and loss of electrical contact within the porous electrode. In addition, there may also be corrosion of adhesives and current collectors that may also lead to decrease in battery capacity.



The most of commercial lithium-ion batteries use graphite as negative electrode material. Side reactions taking place at negative electrode/electrolyte interface play a main role in lithium-ion battery degradation [9,10]. Although solid electrolyte interface (SEI) prevents the graphite from further electrolyte degradation, continuous growth of the SEI layer is obviously detrimental to the cell performance of lithium-ion batteries as lithium is irreversibly consumed and may cause an increase in the overall cell resistance. Moreover, when the SEI layer becomes too thick, some amount of active material can become electrochemically inactive resulting in negative electrode active material loss. It is reported that high temperatures are more detrimental to cell life during storage by activating side reactions. State of charge (SOC) influences also cell calendar life but to a lesser extent; fully lithiated graphite is indeed considered to be unstable because the intercalated lithium tends to diffuse to the graphite edges where it may interact with the solvent components [11].

Nickel-Metal Hydride (Ni-MH) rechargeable batteries have several advantages over conventional lead-acid and nickel-cadmium batteries due to no concentration change of the electrolyte, high-energy density, the capability of overdischarging and overcharging, and the absence of toxic heavy metals [12]. However, the aging rate is relatively higher than that of the Nickel-Cadmium (Ni-Cd) batteries [13], which is disadvantageous for practical applications. Aging of Ni-MH batteries over time, arises from the reaction of the residual hydrogen with the positive electrode, the slow decomposition of electrodes, and the shuttle effect of impurity ions such as nitrates from the separator or sintered positive electrode [14-16].

In this work, the calendar aging behaviors of a commercial graphite/lithium-nickel-manganese-cobalt-oxide (LNMC) lithium-ion batteries [17] (Manufactured by ASPILSAN Energy, labeled 4411-4711, 3.25 Ah and 7.5 V) and Ni-MH batteries [18] (Manufactured by ASPILSAN Energy, labeled 4011-4014, 2.30 Ah, 7.2 V) are investigated, which includes the effect of temperature and storage time. The purpose of the present research is to find proper storage temperature range of the batteries.

2. Experimental

For the calendar aging, a commercial graphite/LNMC Lithium-Ion batteries labeled 4411-4711 was charged using with ASELNAN 4400 Lithium-Ion Battery Charger. Ni-MH batteries labeled 4011-4014 was charged using with ASELNAN 4011 Ni-MH Battery Charger [19]. Calendar aging tests were performed by storing them at -20°C, 20°C and 55°C temperatures and open circuit voltages related to 100% SOC initially. During storage, no trickle charge was applied and battery voltage was free to change between two characterization segments. Batteries and charger devices are shown in Figure 1.

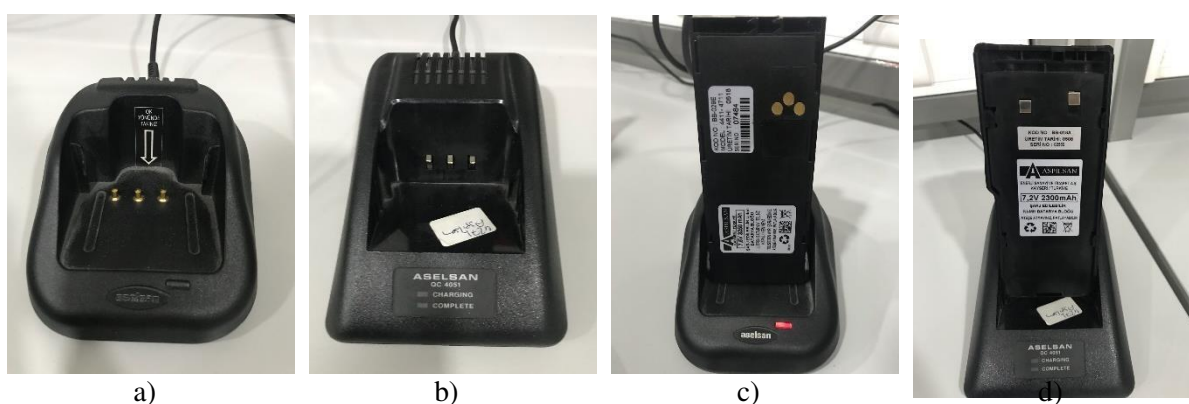


Figure 1. a) ASELNAN 4400 Li-Ion Battery Charger, b) ASELNAN 4011 Ni-MH Battery Charger, c) ASPILSAN 4411-4711 battery charging d) ASPILSAN 4011-4014 battery charging.

At each temperature, two batteries were tested in order to prove the reproducibility of the measurement. To find the aging of batteries, the capacity measurements were carried out at the beginning of test, at the end of the test and in the intervals of four weeks. Electrochemical capacity measurements were performed at room temperature using a special battery cycler (ASPILSAN Energy). To determine the capacity of Li-Ion batteries, a standard charge (C/3 constant current charge to 100% SOC (8.4 V), a constant voltage (8.4 V) charge until the current was below C/10 rate), followed by 1C discharge (down to 6.4 V) measurements were carried out. To determine the capacity of Ni-MH batteries, a standard charge (C/2 constant current charge to 100% SOC (11.0 V)), followed by C/2 discharge (down to 6.0 V) measurements were carried out.

After placing the batteries at 100% SOC and desired temperature and allowing to stand for 4 weeks of time, then discharge them to determine apparent capacity loss followed by one cycle charge/discharge to find the permanent capacity (irreversible capacity) loss. The reversible capacity (self discharge) loss was calculated by taking the difference between the apparent capacity and irreversible capacity losses. Capacity loss tests were performed using Digatron BTS500 battery test system [20].

3. Results and Discussion

Figure 2 shows the effect of temperature on the apparent capacity losses of Li-Ion and Ni-MH batteries. It can be seen from Fig. 1 that the apparent capacity losses of Li-Ion and Ni-MH batteries depend on the temperature at which they are stored; the higher the temperature, the greater the apparent capacity loss of the batteries. Li-Ion and Ni-MH batteries stored at -20°C and 20°C will lose up to 6 % of their charge within 4 weeks. If they are stored at a higher temperature (55°C), they will lose the charge at an even higher rate (9 % for Li-Ion and 24 % for Ni-MH).

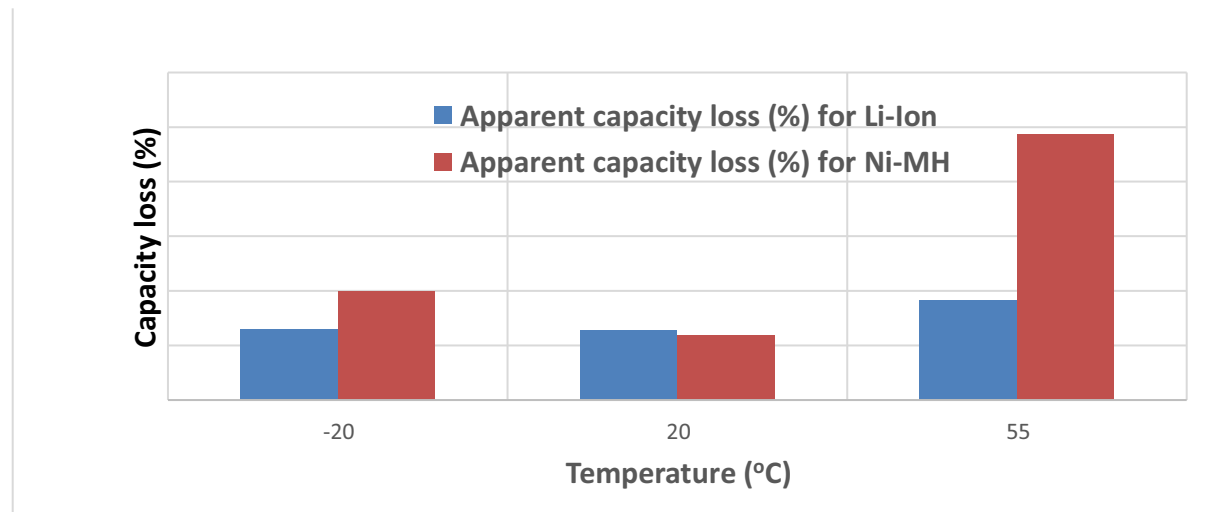


Figure 2. Variation of apparent capacity loss with temperature for both Li-Ion and Ni-MH batteries stored for 4 weeks at different temperatures.

4. Conclusion

Apparent capacity losses of Li-Ion and Ni-MH batteries under different temperature and 100% SOC conditions were investigated. The apparent capacity losses of the batteries increase with increasing the temperature.

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