Reliability Evaluation of Li/SOCl₂ Battery for Smart Electricity Meter Based on Remaining Capacity

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Abstract. The life and reliability of the battery are the keys to ensuring smart electricity meters function properly during a power outage. This paper aims to study the capacity prediction and reliability evaluation methods of lithium thionyl chloride batteries for smart electricity meters based on capacity degradation model. The mechanism of capacity attenuation of backup lithium battery of smart electricity meters is introduced. An accelerated aging test method is proposed to study the influence of storage time, working condition, and temperature on capacity degradation. A semi data-driven model is used to describe the capacity degradation. According to the mathematical model, battery life under different storage conditions in the working environment of smart meters can be calculated.

1. Introduction
Lithium Thionyl Chloride battery is widely used as a backup power supply for smart electricity meters in China due to its high capacity density and long storage life. However, the clock failure of smart electricity meter caused by the lack of battery capacity is very serious. Therefore, lifetime prediction and reliability evaluation are the key issues.

To solve this problem, building a battery aging model is an effective method. Lithium battery aging models could be classified to semi-empirical[1][2][3], fatigue approach[4][5], and electrochemical models[6][7]. At present, simple methods of life prediction have been reported in the literature, such as the method based on the neural network [8]. These methods rely on the learning test set and cannot infer the situation that is not used in the learning test set. Besides, the physicochemical model focuses on the single aging mechanism, such as the formation of solid electrolyte interface (SEI) [9] [10]. However, these models are complex, difficult to parameterize, and can only describe a single mechanism. [11] has established a parameterized life prediction model for automotive lithium batteries. The research method has reference significance, but its conclusion is only for secondary batteries with specific structures. [12] established a semi-empirical mathematical model according to the degradation law for the residual capacity of coiled Li/SOCl₂ batteries. Besides, there are also studies on establishing the self-discharge equation of Li/SOCl₂ batteries by calorimetry [13]. This method requires an accurate measurement of the calorific value and has higher requirements for the experimental device.

Based on the structure and principle of Li/SOCl₂ battery for smart electricity meter, this paper analyzes the battery capacity fading mechanism and discusses the similarity between the coil cell and
bobbin cell. Aiming at the Li/\text{SOCl}_2 battery for smart electricity meters, an accelerated aging experiment scheme, as well as a method for the model establishment and verification, are proposed. The model can extrapolate the accelerated aging test data to obtain a more accurate capacity prediction. On this basis, considering the battery capacity dispersion, the method of battery reliability evaluation is discussed.

2. Mechanism of capacity fading

2.1. Battery structure and characteristics

The battery used for the smart electricity meter in China is the primary Li/\text{SOCl}_2 battery (ER14250 1/2AA-size bobbin cell). The structure is shown in Figure 1.

![Figure 1. The structure of ER14250.](image)

The battery has the following characteristics:
- Nominal voltage 3.6V (at 0.1 mA + 20°C).
- Operating temperature range - 60°C to + 85°C.
- Low self-discharge rate.
- Low working current.
- High and stable operating voltage.

The electrochemical reaction equation of the battery is as follows. Anodic reaction:

\[
\text{Li} - e \rightarrow \text{Li}^+
\]

(1)

Cathodic reaction:

\[
2\text{SOCl}_2 + 4e \rightarrow \text{SO}_2 + S + 4\text{Cl}^-
\]

(2)

Total reaction:

\[
4\text{Li} + 2\text{SOCl}_2 \rightarrow 4\text{LiCl} + S + \text{SO}_2
\]

(3)

Lithium provides electrons during discharge, Li+ enters the electrolyte and forms LiCl with Cl- generated from the positive electrode. The positive electrode of the battery is a mixture mainly composed of acetylene black and polytetrafluoroethylene, a catalyst for the cathode reaction, and a carrier for the products LiCl and S.

2.2. Capacity fading mechanism

In addition to the reduction in capacity due to the large discharge current caused by poor manufacturing consistency of the hardware circuit, there is also a capacity degradation due to the battery's characteristics. The decomposition of the electrolyte on the anode and cathode and the
formation and growth of the passivation film on the electrode surface is considered to be the main aging processes, leading to reduced capacity and increased resistance.

2.2.1. Reduction in cathode porosity. According to the reaction in Eq. (3), the solid LiCl and undissolved S produced by the reaction may be deposited on the carbon electrode, blocking the pores of the carbon electrode, resulting in a decrease in the effective area of the electrochemical reaction and shortening the battery life. When the porous carbon electrode is blocked, the discharge ends[14]. This causes the electrolyte channel to be blocked, and also increases the non-uniformity of the electrolyte concentration, resulting in capacity loss.

![Figure 2. Carbon electrode before and after discharge.](image)

2.2.2. Formation of the passivation film. The formation of passive film is the main process of capacity degradation in lithium thionyl chloride batteries under open-circuit storage. LiCl film is formed when lithium contacts with electrolyte. There are two types of passivation film: compact layer and sparse layer, as shown in Figure 3. The formation of the secondary film is due to the dissolution and precipitation of the primary film. Due to its porous structure, the secondary film has good electrical conductivity, which is difficult to measure by the electrochemical method. The growth rate of the secondary film depends on temperature, electrolyte concentration, and electrolyte additives.

![Figure 3. Passive film simulated on a 500*500 lattice [15].](image)

The first film next to the lithium electrode can prolong the storage life of the battery and reduce self-discharge. The second film outside it has a loose and porous structure and will continue to grow. The outer film will increase the internal resistance of the battery. When the high current is discharged, the passivation film will be gradually destroyed. The loose porous layer will be destroyed first. As shown in Figure 4, with the increase of the discharge current, the first dense film will gradually be destroyed. The passivation film will increase the internal resistance and prevent the reaction from proceeding, so the voltage hysteresis of the battery will become more obvious as the discharge current increases.
Under low-current discharge, the discharge time is long. Because the discharge current is small, when the thickness of the passivation film is not sufficient to affect the load, the LiCl film will continuously thicken and consume Li, which will affect the battery capacity.

For the coiled cell, as shown in Figure 5. There is a layer of separator between the positive and negative electrodes, which are wound together into a battery cell. The difference between this structure and the one studied in this paper is that the electrode works with two sides. This structure has more load capacity, but it may also make the capacity of the battery decline more seriously at high temperatures. Through the structure analysis, it may be acceptable that, similar to the coiled cell, the formation of the LiCl film is the main capacity degradation process in the bobbin cell, and the aging mechanism is the same in the aging temperature range from room temperature to 70℃. This hypothesis needs to be verified by experiments.

2.2.3. Influence of working mode. When the current is discharged at different rates, the concentration of electrolyte inside the battery will be different. Then when the discharge is terminated at the same voltage, the amount of active materials remaining in the battery will be different, that is, the amount of residual charge is different. The larger the current used for discharging, the less capacity is available when the cut-off voltage is reached. If discontinuous intermittent discharge, the battery discharge capacity will be more, but continuous discharge with the relatively small current will still cause capacity loss[16].

3. Battery reliability evaluation
3.1. Accelerated aging test

In this work, a Li/SOCl\textsubscript{2} bobbin cell (14250) was used with a nominal capacity of 1.2 Ah. Cells with similar structures are typically used in clock backup power applications.

Considering that the power consumption of the battery is very low in a power outage (the low power mode chip consumes 0.2% of its nominal capacity per day), an accelerated aging test is performed on the battery and peripheral circuits. Because the boiling point of the SOCl\textsubscript{2} in the battery is 78.8 °C, to ensure the same aging mechanism, the experimental temperature is selected below this temperature. It can be known from the temperature degradation test conclusions of lithium thionyl chloride batteries with different structures that the capacity degradation index depends on temperature. The relationship between the two can be described by the Arrhenius equation. Therefore, determining the stress level at equal intervals by the reciprocal of the temperature stress is beneficial to improve the accuracy of the test. The temperature was set at 27, 45, 56, and 74 °C. The capacity degradation data at three temperatures (27, 56, and 74 °C) were used to construct the mathematical model, and the degradation data at 45 °C was used to verify the accuracy of the model. Since the discharge of a large number of batteries is relatively time-consuming, to balance the difficulty of model establishment and testing, 4 batteries are set for complete discharge in each test cycle. The test is designed by shortening the measurement interval at high temperature and extending the measurement interval at low temperature, as shown in Table 1.

| Temperature/°C | Number | Test interval/week |
|---------------|--------|--------------------|
| 27            | 16     | 4                  |
| 45            | 24     | 2                  |
| 56            | 48     | 1                  |
| 74            | 48     | 1                  |

The battery is discharged with constant resistance and the load voltage is recorded to calculate the capacity. Electrochemical impedance spectroscopy can also be used to analyze the formation of the battery surface film. Because the discharge capacity varies under different discharge currents, the discharge capacity / initial capacity is selected as the parameter. However, it should be taken into account that due to the difference in individual battery capacity, the specific capacity value will be different under the same percentage of remaining capacity.

To explain the methods and ideas of battery life prediction and reliability evaluation, numerical examples in [12] are listed here. The battery storage capacity degradation data of this case is used for analysis. Accelerated aging experiments can obtain results similar to Figure 6.

![Figure 6. Capacity fade with temperature and time.](image)

![Figure 7. Normalized capacity fades at inverse temperatures (50,60,70°C).](image)
The assumption that the capacity degradation has an exponential relationship with temperature can be determined by the linear trend in Figure 7. According to the same aging mechanism stored under different temperature stresses, the thickening of the passivation film is the basis of the main aging process. Equations used to fit aging data can be established:

\[
\frac{C_{\text{act}}(t,T)}{C_{\text{ini}}(t_0,T)} = 1 + F(t) \cdot B(T)
\]

where \(C_{\text{act}}/C_{\text{ini}}\) is used to describe the change of capacity, and \(F(t)\) is used to describe the influence of time on capacity attenuation:

\[
F(t) = C_a \cdot t^b
\]

\(C_a\) is used to describe the capacity decay rate at the reference temperature \(T_0\). \(B(T)\) is used to describe the effect of temperature on the capacity decay rate:

\[
B(T) = C_T \frac{T - T_0}{\Delta T}
\]

\(C_T\) is a fitting parameter, describing the impact of temperature on capacity degradation. \(T_0\) is the reference temperature, and the setting of its value can be arbitrary. Choose \(T_0 = 27^\circ\text{C}, \Delta T=10^\circ\text{C}\), which means that compared with the reference temperature \(T_0\), every 10°C increase in temperature results in an increase in capacity degradation coefficient \(C_T\).

| Equation | \(R^2\) | Parameter | Value  |
|----------|---------|-----------|--------|
| \(\frac{Cap_{\text{act}}}{Cap_{\text{ini}}} = 1 + C_T \frac{T - T_0}{\Delta T} \cdot C_a \cdot t^{0.5}\) | 0.9504 | \(C_T\) | 1.4189 |
| | | \(C_a\) | -0.0391 |

Table 2. Parameter fitting results.

Use software such as origin and 1stopt for data fitting. The fitting results at various temperatures are shown in Figure 8. The goodness of fit \(R\)-square is used to evaluate the results of model fitting.

![Figure 8](image1)

**Figure 8.** Fitting results for capacity fading.

![Figure 9](image2)

**Figure 9.** Comparison between the model and measurements at 40°C.

The experimental data not involved in the process of establishing the mathematical model were compared with the established model, and the accuracy of the model was determined by the value of \(R^2\). In the data case used, \(R^2=0.9077\).

3.2. Lifetime prediction
The constructed capacity model can predict the remaining battery capacity. Also, analyze numerical cases. Storage at 27°C for 10 years, battery capacity loss of 89.128%, so the annual average self-discharge rate is 8.9%. From the battery discharge experiment data, it can be known that to prevent the load voltage from falling too much under different discharge states, the remaining capacity (to the 2.0V cut-off voltage) should be at least 10% with a margin (under 330Ω discharge, the load voltage starts to drop rapidly when the capacity is about 17%). So, it can’t meet the storage requirements for 10 years. As shown in Table 3, the acceleration factor (AF) defines the ratio of the reference temperature to each temperature when the battery reaches 30% of the initial capacity.

### Table 3. Predicted lifetime and AF at different temperatures.

| Temperature/°C | Storage time/weeks | AF |
|----------------|-------------------|----|
| 27             | 320.75            | 1.0|
| 30             | 260               | 1.23|
| 40             | 129.13            | 2.48|
| 50             | 64.13             | 5.00|
| 60             | 31.85             | 10.07|
| 70             | 15.82             | 20.27|

3.3. Reliability evaluation

Analysis of battery capacity distribution in the case. It is assumed that the capacity follows a normal distribution and does not change during aging. Take the difference between the maximum and minimum battery capacity in the numerical case as 6σ. The initial battery capacity distribution is N (900,184.07). Due to the existence of individual battery differences, the remaining capacity of the battery is different under the same capacity percentage, so the reliability calculation based on the capacity percentage is not rigorous enough. This paper uses 200mAh as the failure threshold and calculates the reliability of the numerical case based on the degradation curve at room temperature. The result is shown in Figure 10. The storage life corresponding to the reliability of 0.9 is about 7.2 years.

![Figure 10. Storage degradation curve.](image)

4. Conclusion

This paper studies the ER14250 battery for smart electricity meters, which mainly includes: battery capacity decay mechanism, lifetime prediction model establishment, and reliability evaluation. Mainly include:

- The capacity fading mechanism of the bobbin cell includes the Reduction in cathode porosity and the formation of LiCl film. Like the coiled cell, The formation of the
passivation film is the main cause of battery capacity degradation, and the capacity degradation mechanism can be considered consistent from room temperature to 78.8°C. 

- An accelerated battery aging test scheme is proposed. The methods of establishing a parameterizable lifetime prediction model and model verification are discussed. This model can be used to evaluate the reliability of the battery, and calculate the remaining capacity, average self-discharge rate and AF of the battery under different storage conditions.

The accelerated aging test is designed for the battery powering the chip, rather than a simple storage experiment. Therefore, the capacity change of the battery under storage and power failure conditions can be studied simultaneously. Besides, the influence of individual battery differences (capacity dispersion) on battery reliability is considered. In future work, further research is needed on the effect of the aging process on the dispersion of battery capacity.

5. References
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Acknowledgments
This work was supported by the National Key R&D Program of China [grant number 2017YFB1300800] and the National Natural Science Foundation of China [grant number 61671172].