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Capacity estimation based on the aging characteristics analysis of Liquid metal batteries

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Abstract-- **The liquid metal battery is a new energy storage technology that is gaining increasing attention due to its high safety and long life. Accurate capacity estimation is crucial for health diagnosis and pack management, providing a strong guarantee of long-term stable operation for energy systems. However, owing to the lack of aging analysis traditional methods are difficult to improve the precision in the situation of unpredictable disturbances or fluctuations, such as capacity plunge. This paper proposes a capacity estimation method based on aging features by combining machine learning and filter algorithms, this method can provide an accurate prediction even the LMB is subject to capacity plunge. First, the aging features are extracted using only a tenth of the whole information from the discharge curve and increment capacity (IC) curve. Next, the Long Short Term Memory (LSTM) network is employed to establish the state-space representation between the aging feature and the capacity. The particle filter (PF) is then combined with the state-space representation to predict the capacity. Finally, aging tests are conducted to validate the precision and effectiveness of the proposed hybrid method. These results show that the proposed method can provide robustness as well as accurate capacity prediction.**

Index Terms-- **Capacity estimation, LSTM, Particle filter, Capacity plunge**

I. INTRODUCTION

Liquid metal battery (LMB) [1-2] is an innovative energy storage technology that offers high safety and an extended lifetime at a competitive price, making it ideal for large-scale energy storage applications. Many scholars have studied the material system on liquid metal batteries to improve the performance, including Li||Sb-Sn [3], Li||Bi [4] , Li||Sb [5], Na-based LMB [6] and so on. In addition to material system, the researches of management are also vital research for the large-scale application of LMB. In LMB models, Liu et al established a first-order Thevenin equivalent circuit model using circuit element to represent the polarization [7]. Shi et al proposed a fractional order physics model by simplifying the electrochemical process[8]. In the regard of state of charge (SOC) estimation, Xu et al used a dual fuzzy-based adaptive extended Kalman filter method to estimate SOC, and Wang et al proposed SOC estimation technique based on Gaussian process regression (GPR) [9]. To better control LMBs given to the high working temperature, thermal simulation was conducted by Zhang et al [10]. Capacity estimation is one of the most important functions for battery management, and is necessary for health diagnostic and consistency analysis. However, the researches of cell aging and capacity estimate for LMBs are extremely lacking. It brings huge obstacles for the storage application of LMBs.

In application, the real capacity is difficult to measurement which depends on the supervision of full charge/discharge process. It is widely accepted that extract features related to aging is indispensable for reducing the computation of and improving precision. Severson et al. [11] used discharge voltage curves from early cycles yet to extract eleven capacity degradation features and applied machine-learning tools to both predict and classify cells by cycle life, achieving 9.1% test error for quantitatively predicting cycle life using the first 100 cycles. Zhao et al [12] extracted thirty-nine domain features from the reconstructed segments of battery charging progress, and these features were applied to predict battery capacity for electric vehicles by the framework comprised of four base learning models. Dai et al [13]choose eight features from the discharge curve and IC peak, and then prior knowledge-based neural network was employed to predict the health state. Lyu et.al [14] combined the Gaussian process regressions (GPR) and Particle Filter (PF) to predict the cell capacity. Two representative battery aging features are extracted from the partial incremental capacity curve smoothed by Locally Weighted Scatterplot Smoothing in this prediction process.

These methods are primarily to construct nonlinear fitting for a large number features and capacity degradation, which have had an incredible effect. However, the aging mechanism of LMBs is entirely different from that of lithium-ion batteries. Therefore, extracting aging features should take into account the evolution rule of the LMBs. Additionally, these methods require training with a large mount batteries dataset, which is currently challenging to achieve. The primary reason for this is the ultra-long life of LMBs, which makes it difficult to obtain sufficient battery datasets. It always need several years to cycle a LMB. Especially, the battery we present in section 2 has been cycling two years, which still has a good discharge performance. So how to make full use of the history dataset to predict the future aging path is vital for LMBs.

Based on the above analysis, this paper proposes capacity prediction methods using historical dataset based on the aging feature and hybrid data-driven methods. To begin with, we established a state function between historical capacity and future capacity using Long Short Term Memory(LSTM) methods. Then we extract aging

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features from the discharge curve and increment capacity (IC) curve, and construct a nonlinear relationship between capacity and aging features using Multi-Output LSTM (MOLSTM). This relationship can be treated as an observation equation. Afterwards, particle filter (PF) are used to update the state equations and observation equations. The rest of this paper is outlined as follows. Section 2 introduces the experiment and methods of aging feature extraction. Section 3 presents the technology of prediction framework. Section 4 discusses the verification results. And the conclusion is drawn in Section 5.

II. EXTRACTION OF AGING FEATURES

This section will detailed introduce the structure of LMB and the test system. The aging feature extraction is also presented in this section.

A. Experiment setup and dataset

Sb-Sn alloys have been reported as environmentally friendly positive electrodes for high-performance LMBs [3]. Figure 1 illustrates the structure and actual product of a 20Ah Li||Sb-Sn LMB. The LMB comprises a negative electrode made of lithium soaked in nickel foam, a positive electrode made of an alloy (Sb-Sn), and a molten salt electrolyte. At the operating temperature, all of the materials become liquids and self-segregate into three layers due to differences in density [8]. This natural self-segregation of electrodes and electrolyte eliminates the need for a diaphragm, resulting in a simple structure that can be easily scaled up. Additionally, the LMB's liquid design eliminates degradation phenomena such as active material loss and lithium plating, resulting in an ultra-long cycle life.

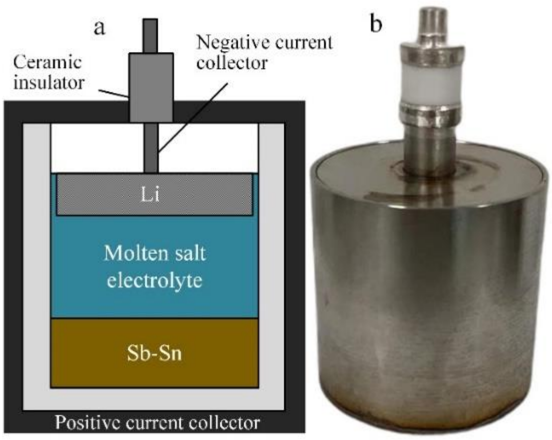

Figure 1 The structure of a 20Ah Li||Sb-Sn LMB (not to scale)

The Test platform is shown in Figure 2. In this study, a 20Ah LMB was used as an experimental subject, which was put into the electric stove to keep a constant temperature. The working temperature is set as 550℃. To record all the battery data, the cell was real-time monitored by the test system, which transfer all the data to the Host PC.

Figure 3(a) presents the capacity aging curve obtained from the aging test, which shows that the LMB has a long cycle life with a capacity retention rate of 91% after 10,000 cycles. In particular, there is a relatively large capacity drops at around 3200 cycles, which is referred to as capacity plunge. Unfortunately, the capacity plunge is unpredictable and is related with the internal reaction of LMBs, which can pose significant challenges for prediction models. Therefore, the prediction model should be designed considering such sudden drops.

Figure 3(b) shows the discharge curve of a fresh cell, indicating the presence of a turning point in the discharge curve. The turning point corresponds to the process of phase transfer. During the discharge process, Li crosses the molten salt and alloy with Sb. Before the turning point, the reaction product is Li_xSb ($0<x<3$) and all the components are in a liquid state. At the turning point, Li_2Sb begins to form, and the change in voltage becomes steady, indicating that the LMB is in a solid-liquid phase mixture stage.

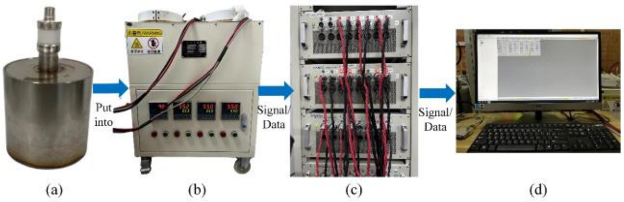

Figure 2 Test equipment (not to scale) (a) 20Ah LMB (b) electric stove (c) Test system (d) Host PC

B. Feature extraction

Aging features are crucial for establishing an accurate model as they can directly reflect the state of cells. However, selecting appropriate features from the many parameters related to cell aging can be challenging. The selection criteria for aging features should consider two key principles. Firstly, the aging features should be easy to obtain in the real application to avoid wasting time and compute resources. Secondly, the aging features must have a strong relationship with cell degradation to enable accurate capacity prediction.

Figure 3(c-e) shows aging features extracted from the discharge capacity and IC (incremental capacity) curve in this study. These features include the voltage of the phase transfer point, the initial discharge voltage and the peak of IC curve. The figure illustrates that the proposed aging features are highly correlated with the available capacity in different aging states. In particular, the reason why these aging features are used are presented as follows:

(1) The voltage of the phase transfer point U_{pt}. The phase transfer point can reflect the active material component. As LMBs aging, the consumption of active material can effect U_{pt}. Specifically, the voltage range of the phase transfer point is between 0.785V to 0.80V, indicating that a small amount of the whole information is sufficient for feature extraction.

(2) The initial discharge voltage U_0. The initial voltage is an intrinsic characteristic of cells that depends on the concentration of active material and internal resistance. However, as the LMB ages, irreversible compounds are produced, which not only consume active material but also increase resistance. Therefore, the initial voltage will decline as the cell cycle progresses.

(3) The peak of IC curve IC_{max}. The IC peak reflect the

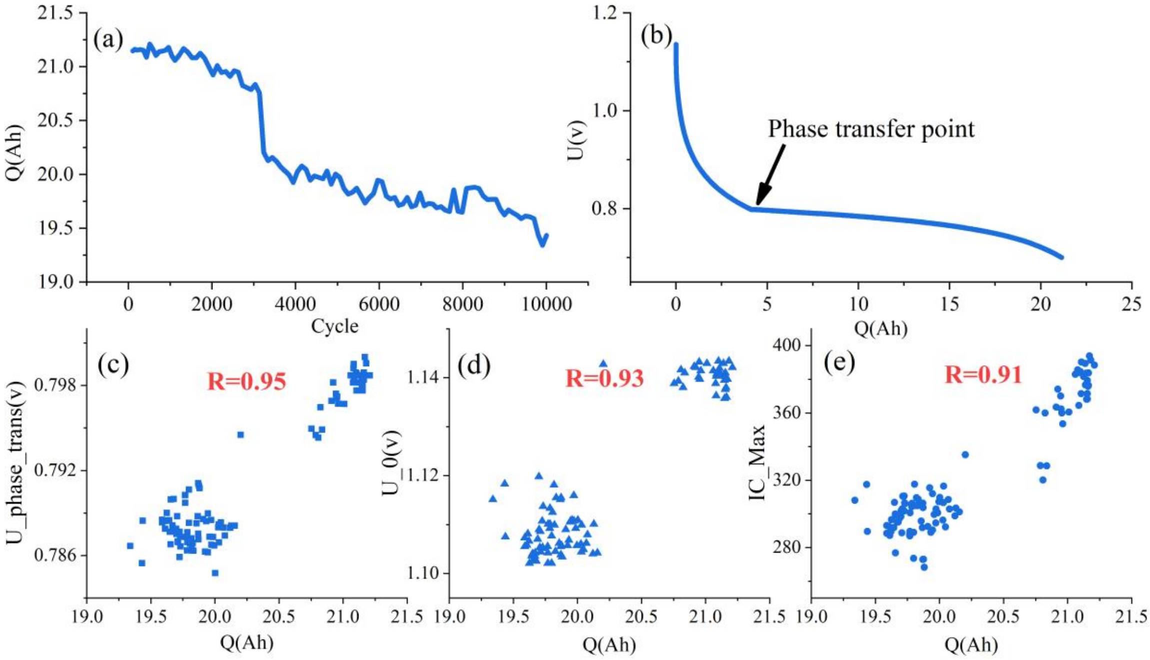

Figure 3: (a) Aging dataset with 20AH LMB; (b) The discharge curve; Aging feature and correlation coefficient with (c) the voltage of the phase transfer point; (d) the initial discharge voltage (e) the peak of IC curve.

capacity change trend in the phase transfer point. Thus, the theory that ICmax change as cell aging is similar to Upt.

III. CAPACITY PREDICTION METHOD FRAMEWORK

This study aims to establish a hybrid data-driven model for predicting available capacity in the situation of capacity plunge. Herein, the state function is constructed by LSTM, and PF is used to track the capacity degradation.

A. State-space equations establish

The process of capacity prediction can be described by a discrete dynamic equation, which is presented as follows:

$$\begin{cases} x_k = f(x_{k-1}, w_{k-1}) \leftrightarrow (a) \\ z_k = g(x_k, v_k) \leftrightarrow (b) \end{cases} \tag{1}$$

In Eq (1), subformula(a) represents the state equation and while subformula(b) denotes the observation equation. Here, x_k represents the state parameter and z_k represent observation parameter. The variable w and v refer to the noise of the state equation and observation equation, respectively; while f and g represent state transition function and observation function, respectively.

As shown in Figure 3(a), the capacity not only degrades overall but also exhibits local fluctuation. Therefore, it is extremely challenging to establish a definitive functional relationship between adjacent capacity data points. To address the capacity prediction problem in this study, LSTM method, shown in Fig 4, is used to construct the state function and observe function. LSTM [15] is a specialized type of RNN that is capable of learning long-term dependencies of datasets. It was developed to tackle the explosion and vanishing gradient problems, which are commonly encountered when training conventional RNNs. LSTM has proven to be effective in a wide range of problems and has become a popular choice in many applications.

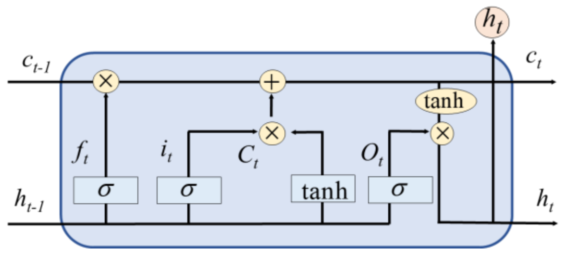

Figure 4 The structure of LSTM

The state equations describing the relationship between adjacent capacity data points can be written as follows:

$$Q_{k+1} = LSTM(Q_k) \tag{2}$$

Where Q_k represents the available capacity in k^{th} cycle. LSTM means the nonlinear function that relates discrete capacity values.

The observation equation is intended to update the unknown state by combining the observe variables in real application. In this study, the aging features extracted in section 2 serve as the observed variables to update the posterior capacity Q_{k+1}. Therefore, the nonlinear function needs to describe the relationship between Q_{k+1} and multi features. To achieve this, we construct a multi-output LSTM, which is presented below

$$\begin{bmatrix} U_{pt} \\ U_0 \\ IC_{\max} \end{bmatrix} = MOLSTM(Q_{k+1}) \tag{3}$$

B. Particle filter-based prediction

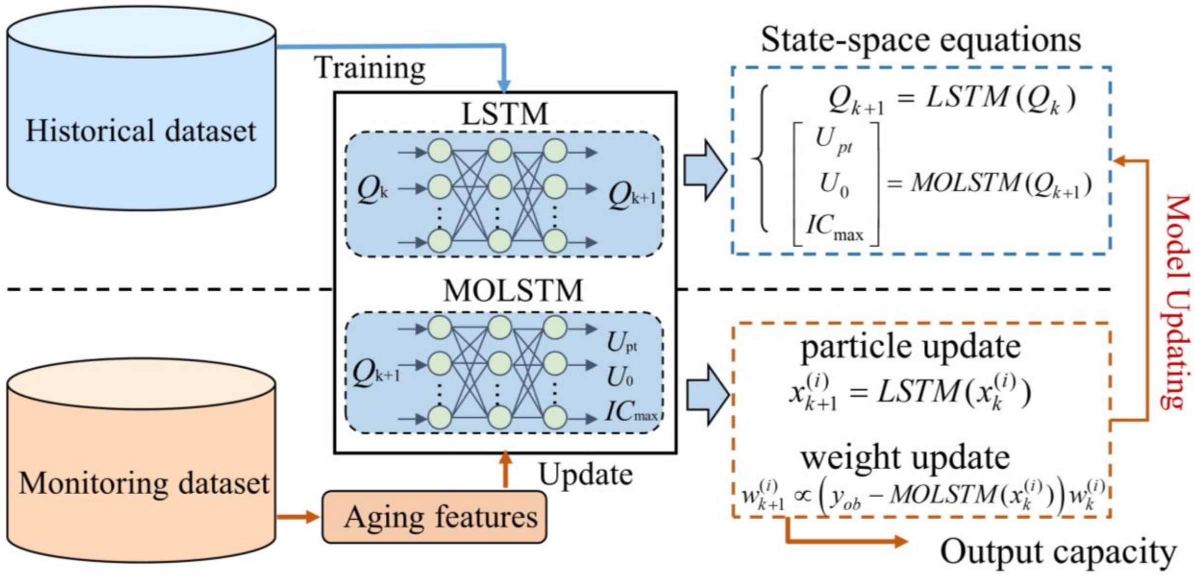

Figure 5: The capacity prediction method framework

PF [16] is a Sequential Monte Carlo method that enables online learning within a Bayesian framework.[17] Bayesian filter methods typically require the calculation of complicated infinite integrals, which can be challenging to compute in the absence of a probability density distribution. Therefore, some filter methods, such as the Kalman filter(KF), Extended Kalman filter (EKF) [18], Unscented Kalman filter (UKF) [19], have been developed on the basic of Bayesian filter. PF is designed to calculate the non-linear state-space equations and has proven to be effective in solving non-linear problems. The basic idea of PF is to use a set of random particles with associated weights to represent the posterior density. The particles and weights will update when the model receives new observe value. The framework for capacity prediction is illustrated in Fig 5.

The proposed PFLSTM in this study can be divided into the following steps:

(1) Model training. Based on the analysis presented in section 1, we need to construct the data-driven model using historical dataset and then update it by sampling aging features. However, the capacity plunge poses a significant challenge to the prediction model. To evaluate the accuracy of the model under sudden condition, we chose 4000^{th} cycle as a node where the capacity just undergoes an abrupt change. Therefore, Therefore, we selected the dataset of the first 4000 cycles as the historical training dataset and extracted aging features and capacity from it. Then according to Eq(2-3), we established state and observation equations. The state equation reflects the capacity degradation trend while the observation equation captures the relationship between the aging features and capacity.

(2) Capacity prediction. PF is used to predict capacity when the model is established. It uses a set of particles, each representing a possible state of the system, to estimate the current state based on the available measurements. Firstly, some particles with weights are randomly generated to represent probability density. All particles are input into the state equations and the weighted average is the best estimate of state variable. In this study, one hundred particles were chosen. Secondly, Aging feature are exacted online from real-time monitoring dataset. Using these sampling aging features, the particle weights are updated by combing the observation equation. Finally, to solve the problem of updating failure caused by particle degradation, the particles' weights are resampled according to the normalized importance weights.

(3) Model updating. The updated values and weights of the particles replace the old ones, and they are updated with new aging features. This process (Steps 1 to 3) is iterated in a loop until the battery capacity reaches the life threshold.

Based on the steps presented above, the capacity prediction is completed.

IV. RESULTS AND DISCUSSION

Based on the framework presented above, the capacity of 20AH LMB is predicted and the results are shown in Fig 6. To compare the rationality of updating models based on aging features, we also used an LSTM without combining PF to predict the capacity.

The Fig 6(a) illustrates the predicted capacity trajectory while Fig 6(b) presents the error results. As shown in this figure, it is clear that the proposed PFLSTM provides better predictions. Based on these results, we can make some observations.

(1) Because we picked the data node immediately after the capacity plunge, it indeed brings significant challenging to the prediction model. The aging trajectory predicted by LSTM deviates from the actual trajectory. However, the proposed PFLSTM can capture the sudden change accurately. Specifically, the Root-Mean-Square Error (RMSE) of LSTM is 0.407AH while PFLSTM provides a prediction with an RMSE 0.109AH. The proposed method improved the performance almost

fourfold in situations where there was a capacity plunge. It represents that the proposed framework can capture more aging information than the individual data-driven method.

(2) The maximum error (ME) of PFLSTM prediction is 0.2764AH, which is the initial prediction caused by the random initial value of particles. However, error value will decrease with the model updating, which indicates the good robustness of the model. It also indicates the rationality of the construct of observation equation.

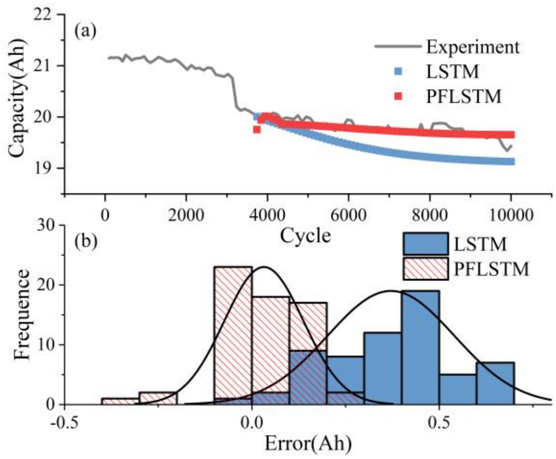

Figure 6: The capacity prediction results and error (after capacity plunge)

Furtherly, we focus on predicting capacity prior to a capacity drop using proposed method in this study. Traditional data-driven method has limited generalization in the absence of sufficient data. However, by incorporating the updating mechanism of a particle filter, we can improve the accuracy and robustness of the method. The results, shown in Figure 7, demonstrate a significant difference between our proposed method and a pure LSTM approach. The LSTM model's prediction deviates significantly from the truth due to the capacity plunge, while our PFLSTM model can accurately capture the trend of capacity fluctuations. This highlights the importance of modeling updating after a capacity drop.

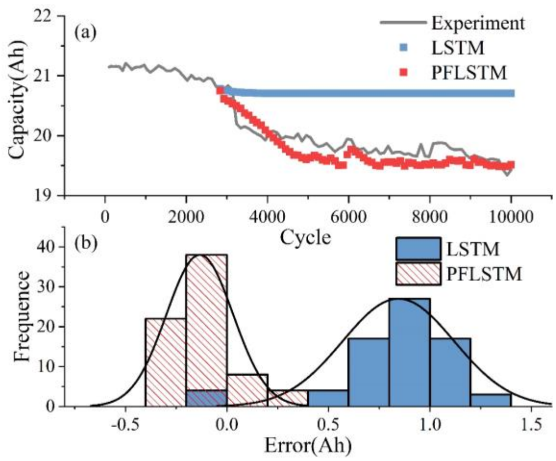

Figure 7: The capacity prediction results and error (after capacity plunge)

The subsequent work will focus on the extracting of aging features. Due to the lack of extensive aging studies on LMBs, the aging process remains unclear recently, posing significant challenging to the future research. Though we have attempted to identify some aging features and analyze the aging mechanism in this study, the operating characteristics of LMBs under high temperatures make it difficult to fully understand the aging process. Therefore, we plan to exact aging features not only from the aging analysis but also from the physics model, which may provide valuable insights for the features studies.

V. CONCLUSIONS

In this paper, a hybrid data-driven framework is proposed to predict the capacity of LMB. Specifically, long short-term memory (LSTM) is used to construct the state-space function, and then particle filtering (PF) is applied to update the state based on the resampling of aging features. This framework strategically integrates the strengths of the data-driven prognostic method and the filtering approach in system state prediction while alleviating their limitations. The results demonstrate that proposed method can effectively and accurately predict capacity with an RMSE of 0.109AH. It represents the potential of the proposed framework for predicting and monitoring the health status and future capacity, which is helpful for the large scale application of LMBs.

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