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## **Prediction of cyclic ageing and storage ageing in a lithium ion battery using an electrochemical model**

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Prediction of ageing for lithium-ion cell is essential. However this is a complicated area with few modelling techniques available. The influence of cycling and storage on capacity fading side reaction is investigated for the first time using an electrochemical model. Thus this paper is a unique attempt towards developing a model which can predict combined cycling and storage. Also this work establishes guideline for calculating the SEI properties based on storage ageing experimentation. Very few works correlated the experimentally observed degradation characteristics with properties of SEI layer or chemical characteristics of a battery. The conventional cyclic ageing correlation cannot be used for storage ageing due to the weak relation of degradation with SoC. In this case, the cycling correlation predicts almost the same degradation at lower SoC and at higher SoC, which is counter intuitive to experimental observations. This limits the applicability of an electrochemical model for HEV storage-cycling drive cycle since the ageing characteristics predicted during the storage time will be erroneous.

In this work, the Pseudo Two Dimensional Model (P2D) equations are modified to include a continuous solvent reduction reaction responsible for capacity fade which is well established and widely applied in previous literatures [1, 2, 3, 4]. The capability of this model to predict the SEI layer growth and internal resistance increase under different operating conditions is carefully used to analyse the storage and cycling reaction contributions. The critical parameter controlling the rate of SEI layer growth is the side reaction coefficient. Another important parameter is the temperature of the battery which is found to accelerate cell ageing. However, in this work, the analysis is limited to isothermal condition since the dependency of temperature on cell operating parameters is complex.

For the cycling test, the cells are cycled between voltage limits at 1.2C discharge and 0.3C charging. Capacity characterisation tests are performed after every 100 cycles. For the storage test, the cells are stored at 25°C and the capacity test has been performed after 73, 139, 202 and 297 days to calculate the remaining capacity left in the cell. The over potential of the side reaction reduces to zero for a storage condition where no external current is applied. Therefore, the intercalation current density reduces to zero. However, the ageing solvent reduction side reaction current density is non-zero for storage. The capacity fading solvent reaction parameters are limited to the interfacial surface area and the side reaction exchange current density. The side reaction coefficient in the electrochemical model is adjusted to match the experimental prediction and conclusions are made based on the variation. The storage condition is also used to fine tune the SEI properties to match the experimental investigations.

Table 1 shows that the modified-side reaction-electrochemical storage ageing model is successful in predicting the degradation characteristics eliminating the influence of other parameters like temperature and DoD. Herein, the storage degradation characteristics of NCA chemistry cell can be captured by two types of correlation, exponential and parabolic, out of which the model with parabolic fit gives higher accuracy which is evident from the validation data presented in Table 1. The parabolic correlation directly takes into account of additional side reactions at 20% SoC into the model therefore, as discussed earlier, introducing more data points into the correlation improves the prediction accuracy to cover the unknown reactions.

Figure 1 shows the model performance on a combined cycling-storage weekday drive cycle. The model is successful in showing the SEI layer growth pattern for different usage conditions like storage, cycling and charging. The rate of SEI growth changes with these conditions; storage and cycling show moderate SEI growth whereas charging shows highest. Therefore, from this analysis, the user can intelligently mitigate against the conditions which have adverse effect on the life of the battery.

Table 1: Error comparison of different ageing models compared to experimental data for different storage SoC

	RMSE (Ah) 20 % SoC	RMSE (Ah) 50 % SoC	RMSE (Ah) 90 % SoC
Independent Reaction	0.018 ( $\pm 0.4$ %)	0.0085 ( $\pm 0.1$ %)	0.0495 ( $\pm 0.8$ %)
Exponential fit	0.072 ( $\pm 1.8$ %)	0.022 ( $\pm 0.5$ %)	0.058 ( $\pm 1.3$ %)
Parabolic fit	0.033 ( $\pm 0.8$ %)	0.013 ( $\pm 0.3$ %)	0.056 ( $\pm 1.2$ %)

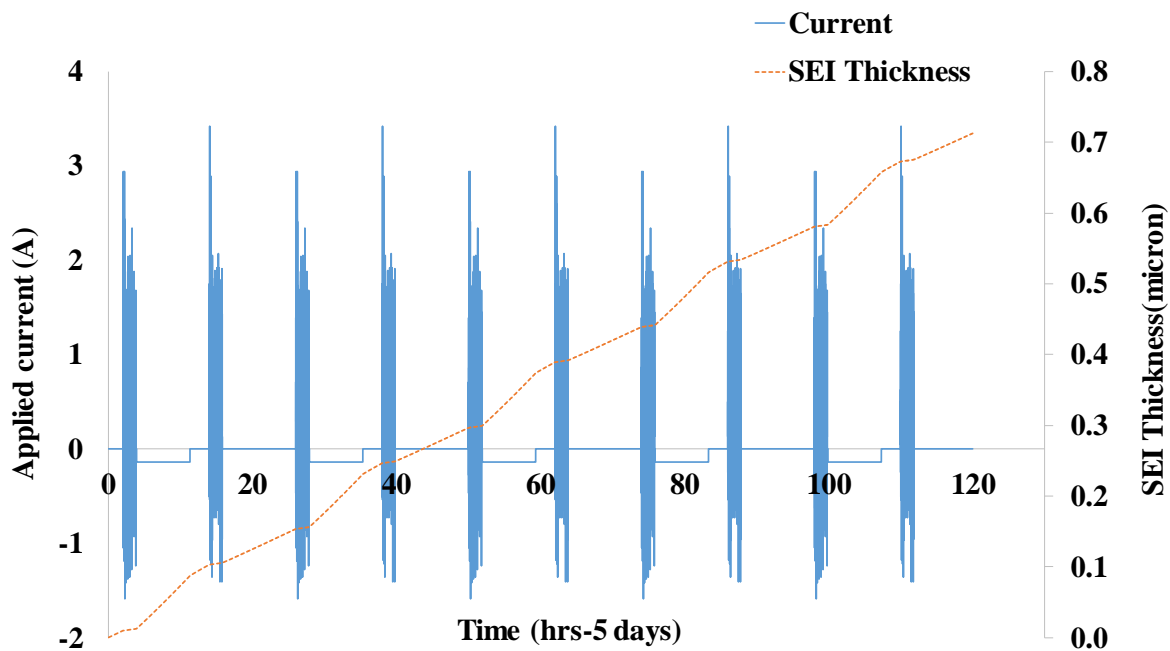


Figure1: Model performance and SEI layer growth pattern with combined cycling- storage drive cycle over a week.

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