Spectral Approach to Li–ion Batteries Degradation Rate Estimation

E A Yusupova, V G Malyshkin, V V Davydov
1Peter the Great Saint–Petersburg Polytechnic University, 195251, Russia
2A.F. Ioffe Physical Technical Institute, Saint Petersburg 194021, Russia

Abstract. Li-ion batteries are critically important component of modern solar power plant systems with over 30% contribution to the total cost. The uncertainty of Li-ion battery degradation rate is a very important risk source of a solar system. The estimation of degradation rate spectrum is an important practical problem. A two stage approach to degradation spectrum estimation is proposed: on the first stage a probability density is constructed, and on the second stage the signal is averaged with the probability density from the first stage. The problem is reduced to matrix spectrum analysis that does not require a $L^2$ norm to minimize. The technique application is demonstrated on two-stage degradation model and commercial Li-ion battery degradation data.

1. Introduction

Li-ion batteries are critically important component of modern solar power plant systems, they typically contribute to over 30% to the total cost. The uncertainty in Li-ion degradation rate is the key economic risk in solar power systems[1, 2]: when a station is built future Li-ion degradation rate has a very high uncertainty, what lead to an uncertainty in the battery lifetime, this makes degradation rate distribution study an important research topic. Because manufacturers provided data is often incomplete or incorrect, the estimation of future degradation rate is of great practical interest for solar power stations.

The degradation of Li–ion batteries is an active field, studied both in terms of applications and theoretical modeling. The term “degradation” can be defined differently. In can be understood as:

- Battery capacity fading, this reduce energy characteristics.
- Internal resistance increase, this reduce power characteristics.
- Increased self-discharge.
- Increased risk of catastrophic failure or even battery fire.

For solar power systems battery capacity fading is the most important degradation aspect (the situation is different for electric vehicles and avionic systems). Battery capacity as a function of cycle number $C(N)$ is typically the most important characteristic in practice. The definition of “cycle” can be rather complex, it includes charge/discharge rate, temperature, humidity and other conditions. There are exist several standards[3–5] where the measurement conditions are specified in details. Among all the specified parameters these two are the most important:

- Current. It is measured in battery capacity $C$. $1C$ means charge/discharge the battery in 1 hour; $2C$ — in 30 minutes. For Li-ion typical testing current is $0.5C$ or $1C$. Batteries, capable of higher current, are seldom. The degradation rate depends strongly on the current.
Temperature. The degradation rate is highly dependent on the temperature. Most often used temperatures are the 20° and 45°. Few manufacturers provide temperature–dependent degradation data. In special applications exploitation temperature range can be critically important characteristic.

Typical $C(N)$ dependence represent two– or four– stages [6] dependence. In in Fig.1 the $C(N)$ for [6] model and for three commercially available batteries is presented. In table I the degradation rate (the number of cycles to 0.8 of the initial capacity) is presented according to manufacturers data. One can clearly see degradation rate increase with current and temperature increase.

### 2. Degradation Rate Spectrum

The $dC/dN$ is the degradation rate. It can vary greatly and is typically obtained by some interpolation technique. A common approach in signal analysis is to represent a signal (in this paper the signal $f = dC/dN$) as a linear superposition of some basis functions (such as Fourier or wavelets[13]). To obtain such a superposition the difference between a signal and interpolating expression is minimized as a $L^2$ norm (least squares) and obtained components are interpreted as projection amplitudes (e.g. Fourier amplitudes), this consists in choosing $Q_k(x) = 0..n − 1$ basis and measure $\langle g(x) \rangle = \int g(x) \omega(x) dx$ (e.g. Fourier basis, orthogonal polynomials, etc.), then for a signal

| Manufacturer   | Model       | Cycles to 0.8          | Wh/L | Wh/kg | W/L  | W/kg |
|----------------|-------------|------------------------|------|-------|------|------|
| A123[10]       | ANR26650    | 6800: (1.2C/2C, 23°)   | 5800 |       | 2600 |      |
|                |             | 1300: (1.2C/2C, 45°)   |      |       |      |      |
|                |             | 670: (1.2C/8C, 45°)    |      |       |      |      |
| LG Chem[9]     | 18650HG2    | 340: (1.3C/3.3C)       | 680  | 240   |      |      |
|                |             | 160: (1.3C/6.6C)      |      |       |      |      |
| Samsung[11]    | ICR18650-22F | 1660: (0.8C/1C, 23°) | 400  | 190   |      |      |
|                |             | 660: (0.8C/1C, 45°)   |      |       |      |      |
|                |             | 330: (0.7C/1C, 60°)   |      |       |      |      |
| EnerDel[12]    | CE175-360 (17.5 Ah) | 6400: (0.5C/0.5C, 0°) | 147  | 1256  |      |      |
|                |             | 2600: (0.5C/0.5C, 30°)|      |       |      |      |
|                |             | 1200: (0.5C/0.5C, 45°)|      |       |      |      |
Consider an alternative. Instead of (1) linear superposition of contributions to \(f\), introduce
\[
\psi(x) = \sum_{j=0}^{n-1} \alpha_j Q_j(x)
\]
as a linear superposition of the basis, and consider the signal weighted with the \(\psi^2(x)\omega(x)dx\) weight:
\[
f_\psi = \frac{\langle \psi^2(x) f \rangle}{\langle \psi^2(x) \rangle} = \sum_{i,j=0}^{n-1} \alpha_i \langle f Q_i Q_j \rangle \alpha_j
\]
(2)

Now, instead of linear superposition to \(f\), we consider linear superposition (defined by \(\alpha_i\)) to \(\psi(x)\), and the square of \(\psi(x)\) provide averaging weight. Any vector \(\alpha_i\) now corresponds to \(f_\psi\), which is a ratio of two quadratic forms on \(\alpha_i\). The approach is now two stage: 1). For a given \(\alpha_i\), build the weight \(\psi^2(x)\omega(x)dx\) 2).Average the signal with this weight to obtain \(f_\psi\) (a ratio of two quadratic forms). The proposed (2) approach is to obtain from the data two matrices: \(\langle f Q_i Q_j \rangle\) and \(\langle Q_i Q_j \rangle\), then, for a given vector \(\alpha_i\), to obtain (2), the signal averaged with \(\psi^2(x)\omega(x)dx\) weight. The key difference is that while the \(\beta_i\) (1) define contributions to the observable \(f\), the \(\alpha_i\) define contributions to \(\psi(x)\) (the square of \(\psi(x)\) define averaging weight to obtain \(f_\psi\)), without any \(L^2\) norm involved[15]. With two matrices obtained from the data the generalized eigenvalues problem:
\[
\sum_{k=0}^{n-1} \langle f Q_j Q_k \rangle \alpha_k^{[i]} = \lambda^{[i]} \sum_{k=0}^{n-1} \langle Q_j Q_k \rangle \alpha_k^{[i]}
\]
(3)

has a unique solution: the unique basis in which both \(\langle f Q_i Q_j \rangle\) and \(\langle Q_i Q_j \rangle\) matrices are simultaneously diagonal. The most important is the interpretation of (3) spectrum. The situation is similar to the one in random matrix theory[16]: to interpret the distribution of (3) eigenvalues \(\lambda^{[i]}\) as a distribution of \(f\).

3. Model Data

For Li-ion battery capacity \(C\), which fade with charge–discharge cycle number \(x = N\), the degradation per cycle typically has several stages similar to those in Fig. 1. The \(C(N)\) is a relaxation type of process, and we are going to use the \(\langle CQ_j Q_k \rangle\) and \(\langle Q_j Q_k \rangle\) matrices in (3) to solve generalized eigenvalues problem (3) as
\[
\sum_{k=0}^{n-1} \langle CQ_j Q_k \rangle \alpha_k^{[i]} = \lambda^{[i]} \sum_{k=0}^{n-1} \langle Q_j Q_k \rangle \alpha_k^{[i]}
\]
then
interpret the distribution of eigenvalues $\lambda^{[i]}$ as the distribution of degradation rates $dC/dN$. In Fig. 2 a model of two-stage degradation rate is presented with different stage lengths. Eigenvalues problem solution give $\lambda^{[i]}$ eigenvalues distribution. The eigenvalues take two values (equal to exact model values) their number is related to the stage length. Changing stages length change only eigenvalues number, not their values.

4. Experimental Data

Consider degradation rate for LG Chem battery[9] shown in Fig. 1. Given the $C(N)$ the $\langle \frac{dC}{dN}Q_iQ_k \rangle$ and $\langle Q_jQ_k \rangle$ matrices are calculated and put to (3). The data is obtained from manufacturer chart by discretization, this limit maximal dimension $n$ in Fig. 3 because of discretization errors. The two–stages degradation is clearly observed. A very important feature of treating $\lambda^{[i]}$ as $dC/dN$ distribution is that all $\lambda^{[i]}$ are finite even when standard definition is infinite. A “proxy for an average” can be obtained as $\frac{1}{n} \sum_{i=0}^{n-1} \lambda^{[i]}$. An important feature of the approach is that the worst/best degradation rate can be directly obtained from the spectrum as minimal/maximal $\lambda$, and used for the estimation of catastrophic degradation risk.

5. Conclusion

Obtaining from the data not a vector $\langle \frac{dC}{dN}Q_i \rangle$, but a matrix $\langle \frac{dC}{dN}Q_iQ_j \rangle$, allows to estimate degradation rate distribution directly, without any apriori assumptions (such as stages number) made by
a human. Mathematically the problem is reduced to matrix generalized eigenvalues problem, not to $L^2$ norm minimization as in Fourier or Laplace.

A novel approach to obtain degradation rate spectrum is developed. Mathematically the problem is reduced not to typically considered interpolation problem, but to matrix spectrum analysis. In this paper the technique is demonstrated for the simplest problem: to obtain $dC/dN$ distribution. However, same technique can be extended to correlate different attributes with each other, even if they do not have the second moment. We can, for example, correlate spikes in $dC/dN$ with the spikes in discharge current. For this task one need to solve the (3) for two signals of interest, then project eigenfunctions on each other. The simplest case $n = 2$ correspond to introduced in ([17]) probability correlation concept $\bar{\rho}(f,g)$, that shows how the probability of low/high $f$ correlates with the probability of low/high $g$; this is different from regular correlation $\rho(f,g)$ (values correlation), that shows how low/high value of $f$ correlates to low/high value of $g$. In contrast with values correlation, probability correlation can be applied to the signals with spikes, what make the answer especially advantageous in situations, where the fact of spike carry the most important information, and the magnitude of spikes is less important.

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