



## Fast formation cycling for lithium ion batteries



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### HIGHLIGHTS

- A fast formation protocol was developed to shorten formation time by a factor of 3×.
- Long-term capacity retention increased after implementation of the new protocol.
- Surface film and charge transfer resistances were reduced with this formation.

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### ABSTRACT

The formation process for lithium ion batteries typically takes several days or more, and it is necessary for providing a stable solid electrolyte interphase on the anode (at low potentials vs. Li/Li<sup>+</sup>) for preventing irreversible consumption of electrolyte and lithium ions. An analogous layer known as the cathode electrolyte interphase layer forms at the cathode at high potentials vs. Li/Li<sup>+</sup>. However, several days, or even up to a week, of these processes result in either lower LIB production rates or a prohibitively large size of charging-discharging equipment and space (i.e. excessive capital cost). In this study, a fast and effective electrolyte interphase formation protocol is proposed and compared with an Oak Ridge National Laboratory baseline protocol. Graphite, NMC 532, and 1.2 M LiPF<sub>6</sub> in ethylene carbonate: diethyl carbonate were used as anodes, cathodes, and electrolytes, respectively. Results from electrochemical impedance spectroscopy show the new protocol reduced surface film (electrolyte interphase) resistances, and 1300 aging cycles show an improvement in capacity retention.

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## 1. Introduction

Lithium-ion batteries (LIBs) are common power sources for portable electric devices and attractive for electric vehicle applications [1,2]. Increasing energy density of LIBs has been a major focus of recent research, with many scientists developing and improving cathode materials (e.g. higher nickel contents) and anode materials (e.g. silicon or tin composites) for high voltage and high energy LIBs [3]. Concurrently, reducing LIB production cost without sacrificing cell performance is another focus especially for electrical vehicle applications [4,5]. The largest contributor to processing cost during LIB production is the electrolyte interphase formation step [4,6].

The anode solid electrolyte interphase (SEI) and cathode

electrolyte interphase (CEI) form when the electrolyte is accessible to electrons at the electrode and, simultaneously the electrolyte experiences an unstable voltage range [7]. During a charging cycle, the electrolyte decomposes and precipitates at low potentials at the anode via reduction reactions and at high potential on cathode via oxidation reactions. Irreversible capacity loss indicating electrolyte interphase formation is the highest after the first charge/discharge cycle (ca. 10% in the case of graphite anode), significantly lower after the second cycle, and even lower after the third cycle and so on (less than 0.05%). The irreversible capacity loss varies depending on negative-to-positive capacity ratio, surface area of particles, operation conditions, etc. [8] Most electrolyte interphase forms during the first charge/discharge cycle because the pristine anode and cathode do not have previously formed passivation layers that electronically insulate the electrode from the electrolyte. If after the first cycle, the anode graphite was not significantly exfoliated, further cycling results in significantly lower electrolyte interphase formation because the preformed interphase layer (from the first

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charging cycle) impedes solvent molecule diffusion towards the electrode surface and electron transfer between the electrode and electrolyte.

Besides material cost, according to Wood et al. [4], the electrolyte wetting and SEI formation steps are the most expensive processes (\$2.2/kWh for electrode processing and \$7.5/kWh for wetting/formation cycling) because of the slow wetting and slow charge/discharge rates (e.g. 3–5 cycles at C-rate of C/20 and 3–5 cycles at higher C-rate at a higher temperature). This process may take up to 1.5–3 weeks, depending on the cell manufacturer and cell chemistry, requiring a tremendous number of charge/discharge cycles for mass production of LIBs, large floor space, and intense energy for the cyclers and environmental chambers. These processes are a major production bottleneck; therefore, it is important to reduce wetting and formation time for cost and production rate benefits.

There have been several electrolyte interphase formation studies that attempted to reduce the required time. For example, skipping the high state-of-charge (SOC) region reduced formation time, but it also resulted in a decrease in capacity retention [9]. Increasing C-rates also reduced formation time. However, it generally caused negative effects on electrolyte interphase formation such as non-uniform thickness and discontinuity of the layer on the anode [10,11]. Formation at high voltage (4.2 V) has rarely been reported, although high-voltage operation is beneficial for high-energy batteries.

In this study, Oak Ridge National Laboratory (ORNL) baseline protocol with different C-rates were evaluated with high-voltage cells (graphite as anodes and layered oxides, NMC 532, as cathodes) and compared with the new protocol, which not only reduced formation time, but also increased cell capacity retention. A simple wetting process was applied in this study. C-rate tests, aging tests, and performance checks during aging were conducted for six different formation protocols (three baseline protocols and three alternative protocols). Electrochemical impedance spectroscopy (EIS) was also measured to investigate total resistance and resistance components.

## 2. Proposed formation method

As the electrolyte becomes unstable during cell charging, in this study, it was hypothesized that:

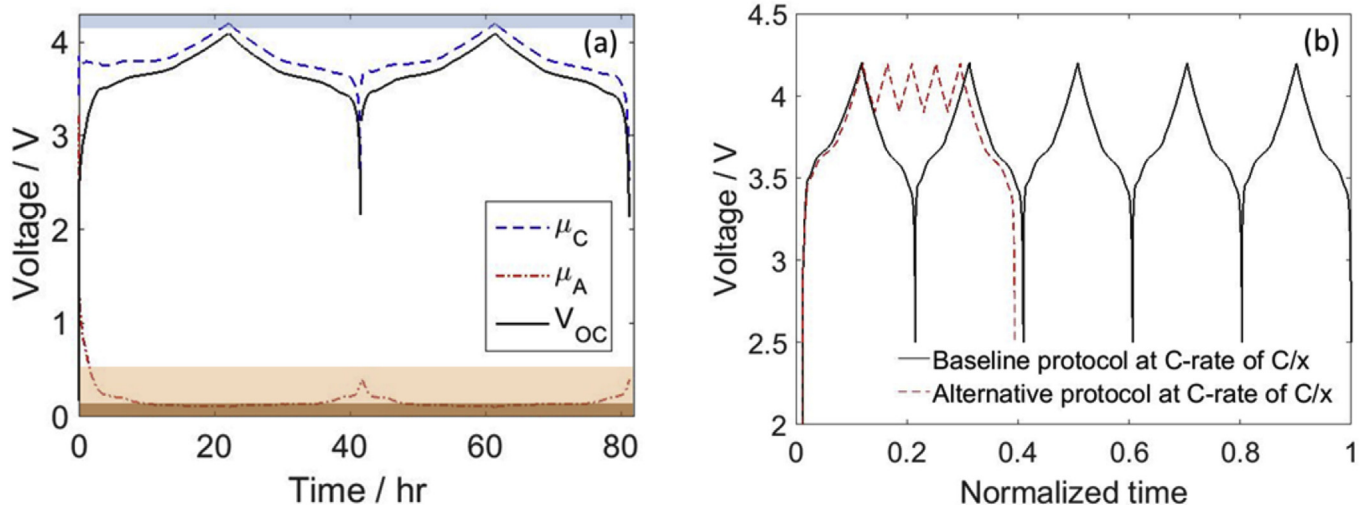
- 1) Most SEI and CEI form at a high SOC because electrolytes undergo more reduction reactions at anode and more oxidation reactions at cathode [12].
- 2) An anode SEI layer at high SOC is more compact and stable than that at low SOC because the potentials at high SOC result in more electrolyte instability and more lithium is available at the anode for reduction with bulk compounds [13].
- 3) The SOC should remain high for a longer period of time and low for a shorter period of time in order to have a compact and stable electrolyte interphase layer, but the SOC should not simply be held at a higher cut-off voltage that results in the current (electron-flow) dropping down to nearly zero.

Typical potential profiles (cathode denoted as  $\mu_C$ , anode denoted as  $\mu_A$ , and potential difference between anode and cathode denoted as  $V_{OC}$ ) from a three-electrode pouch cell (graphite/Li/Li<sub>1.02</sub>Ni<sub>0.50</sub>Mn<sub>0.29</sub>Co<sub>0.19</sub>O<sub>2</sub>) are illustrated in Fig. 1a showing the unstable potential ranges of the cathode [14] (light blue zone) and anode (light orange zone and dark orange zone). The color intensity indicates the relative degree of instability of the electrolyte. Based on the hypothesis of this study, an alternative protocol for electrolyte interphase formation in Fig. 1b is shown and compared with a baseline protocol, the latter of which consists of a series of charge and discharge cycles at a constant C-rate without any interruption between the lower and upper cut-off voltages. The alternative protocol, however, involves repeated cycling within a high SOC region (after the first charge) until the last cycle where a full discharge takes place.

In this study, the baseline formation protocol was evaluated with three different equal charge and discharge C-rates: C/20, C/10, and C/5. Rates of C/20 or C/10 are generally used for at least the first formation cycle in standard cell manufacturing. The baseline formation protocols were compared with the alternative protocols using the same three equal charging and discharging C-rates: C/20, C/10, and C/5. Abbreviations used in this study are listed with their respective descriptions in Table 1. Prior to beginning all formation cycling, each cell was exposed to a 3-h electrolyte wetting process.

## 3. Experimental

Eighteen ~1.5 Ah pouch cells were assembled for testing using the six different formation protocols (three pouch cells were used



**Fig. 1.** Typical cathode potential ( $\mu_C$ ), anode potential ( $\mu_A$ ), and voltage between anode and cathode ( $V_{OC}$ ) from a three-electrode pouch cell (graphite anode/Li reference/Li<sub>1.02</sub>Ni<sub>0.50</sub>Mn<sub>0.29</sub>Co<sub>0.19</sub>O<sub>2</sub> cathode) with potential ranges in blue and orange regions where the electrolyte is not stable (a); cell voltage profiles from a baseline and alternative (subject of this study) SEI formation protocol (b). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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