



# A reduced order electrochemical and thermal model for a pouch type lithium ion polymer battery with $\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2/\text{LiFePO}_4$ blended cathode



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## HIGHLIGHTS

- Reduced order model for cells with blended cathode of NMC and LFP.
- Model validation with experimental results of voltage, SOC, and heat generation rate.
- Analysis each active material's contribution to cell performance.

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## ABSTRACT

$\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$  (NMC) and  $\text{LiFePO}_4$  (LFP) as a cathode material have been widely employed for cells designed for high power applications. However, NMC needs further improvements in rate capability and stability that can be accomplished by blending it with LFP. Working mechanism of the blended cells is very complex and hard to understand. In addition, characteristics of the blended cells, particularly the plateau and path dependence of LFP materials, make it extremely difficult to estimate the state of charge and state of health using classical electric equivalent circuit models. Therefore, a reduced order model based on electrochemical and thermal principles is developed with objectives for real time applications and validated against experimental data collected from a large format pouch type of lithium ion polymer battery. The model for LFP is based on a shrinking core model along with moving boundary and then integrated into NMC model. Responses of the model that include SOC estimation and responses of current and voltage are compared with those of experiments at CC/CV charging and CC discharging along with different current rates and temperatures. In addition, the model is used to analyze effects of mass ratios between two materials on terminal voltage and heat generation rate.

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## 1. Introduction

Conversion efficiency of future power systems used in grids or transportation systems can be substantially improved by storing excess energy and retrieving it that would otherwise be dissipated. Particularly, batteries are preferred as energy storage because of their high efficiency during charging and discharging processes as well as their high power and energy density compared to other alternative storage technologies. Among different battery

technologies, the Lithium ion polymer battery (LiPB) is the most preferred technology simply because of its high power density and the high number of cells that are currently being produced for consumer electronics. The same chemistries for electrodes and minimally modified electrolytes can still be used to design cells for high power applications. However, the packaging can be differently. Depending on the method of packaging, batteries can have a cylindrical, prismatic, or pouch shape. Since the current rates are relative high in the applications, heat generated in the cells becomes high, too, which accelerates side reactions and degradations. As a result, a structural design is required, which includes a relatively high heat transfer capability in addition to massive manufacturability. Therefore, the large format pouch cells are widely used for these high power applications.

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Anodic materials used for those cells are basically carbon graphite, while different cathode materials are chosen to meet performances of the cells, including a blended chemistry [1]. Several basic cathode materials with extra additives have been made to design either high power or energy cells with safe functionalities and long cycle life considering low manufacturing costs. The major materials with structures are as follows;  $\text{LiFePO}_4$  (LFP) with one dimensional olivine structure,  $\text{LiCO}_2$  (LCO),  $\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$  (NMC), and  $\text{LiNi}_x\text{Co}_y\text{Al}_{1-x-y}\text{O}_2$  (NCA) with two dimensional layered structure, and  $\text{LiMn}_2\text{O}_4$  (LMO) with three dimensional spinel structure.

Advantages of the LFP are electrochemical and thermal stability compared to others, the safety can be improved. In addition to a long cycle life, a high rate capability employing nanoparticles can be accomplished. However, the materials show a relatively low capacity (160 Ah/kg) along with a low standard voltage of 3.4 V vs. Li in addition to the voltage plateau caused by two-phase transition during lithiation and delithiation in LFP particles [2].

The other materials, LCO, NMC, and NCA with 2D layered structures have a high capacity and a high standard voltage, but do not show electrochemical and thermal stability in operations. LCO shows the lowest thermal stability, especially when overcharged with a voltage that is larger than 4.2 V. Other components like Al and Mn in NCA and NMC can chemically stabilize the cathode, but cycle life and safety still remain incompletely solved [3,4].

Conversely, LMO with 3D spinel structure is promising with technical advantages of high voltage, high power, good safety, and low cost. However, the manganese can be dissolved in electrolytes, which reduces cycle life and deteriorates safety, and the dissolution is accelerated by elevated temperature. In addition, the capacity and energy density are relatively low and their typical values are about 100–120 Ah/kg and 380 Wh/kg, respectively [1].

Analysis above shows that there is no single chemistry for cathode that provides all of requirements for electric vehicle applications. Blending different chemistries is the potential solution for designers to get around drawbacks and maximize the advantages, as summarized in Fig. 1.

### 1.1. Review of blended cathode materials

Cathode materials of batteries applied for xEVs should ideally facilitate high capacity, power, energy, rate capability along with good safety, long life at low costs. However none of the single cathode materials can meet all of the requirements above as discussed previously. Blended cathode materials can complement each other and achieve better performance than a single parent cathode material.

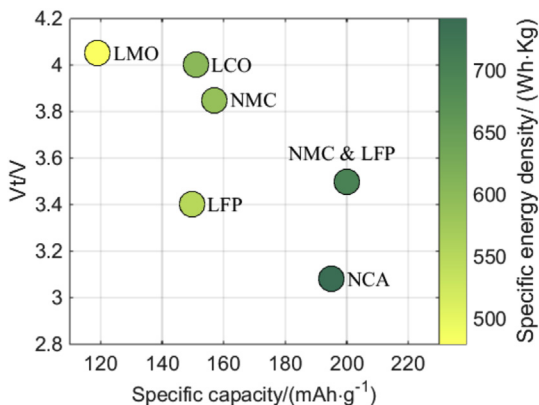


Fig. 1. Performance of cathode materials.

As a matter of fact, LMO is one of favorite cathode materials that can provide high power and rate capability along with increased safety. The demerits of the materials can be improved by blending them with the materials capable of providing high capacity or stabilizing them by preventing from Mn dissolutions. A blended cathode material made of LMO and NCA proposed shows improved performances in increased discharge capacity and reduced heat generation in addition to decreased Mn dissolution. An optimal ratio of NCA for the best performance is 33.3% [5]. In addition, different ratios of LMO and NCA can also achieve improved performances in rate capability, and combined power and energy [6]. Other study shows that blending the LMO with  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  can decrease capacity fade of LMO because of reduced dissolution of Mn into the electrolyte, even at elevated temperatures [7]. The optimal ratio for  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  that completely prevents the dissolution was 15wt%. Structure of cathode materials has been investigated to suppress Mn dissolution and to retain the capacity. The layered oxide cathode such as LCO turned out to be the best performing structure [8]. Contribution of different materials to the cell capacity and structural changes of the mixed LMO and NMC are also investigated using *in situ* X-ray Diffraction (XRD). Based on results for structure changes of each materials during operations, optimal ratio of materials are suggested, which improves the cell capacity [9].

On the other hand, LCO is widely employed as cathode materials for batteries used for portable electronic devices because of high capacity and energy density along with long cycle life. However, poor thermal stability of LCO has raised concerns about safety, especially when being overcharged. This thermal stability can be improved by blending LCO with NMC, whose surfaces are coated with  $\text{AlF}_3$ . The modified blended cells show not only improved thermal stability, but also high discharge capacity along with good capacity retention rate [10]. Olivine-structured LFP has been used as an additive for cathode, which also improves the thermal stability of LCO. The LCO/LFP/Al double-layered cathode showed the best tolerance against overcharging and improved safety compared to that of LCO [11].

In addition to the requirements for increased capacity and power density along with high safety, the high rate capability is also an important criteria, which can be achieved using LFP material. LFP as a cathode material has shown a high stability in electrochemical and thermal aspects and a high rate capability, but a low standard potential against Li electrode that is pretty flat around 3.4 V. These drawbacks can be improved by blending it with other materials that have a layered oxide structure.

Two different cathode materials made of LFP/NMC and LFP/LCO are compared each other. The first one has shown superior performance in cycling with high current rates, while the others with layered configuration has shown better in rate capacity because of LCO performance in both good rate capability and high energy density [12]. A different configuration for two materials is proposed, that is made of NMC as the core coated by LFP [13]. The NMC has a high capacity and energy density, but a poor cycle retention at elevated temperature, while LFP has a low energy density but a high thermal stability. The results have shown that the coating using LFP significantly improves cycling performance of NMC at high temperatures without a large initial capacity drop in the first cycle. Furthermore, a blended cathode composed of  $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNi}_{0.44}\text{Mn}_{0.31}\text{Co}_{0.25}\text{O}_2$  (ANL-NMC, with  $x = 0.5$ ) and LFP is proposed [14], which has increased both energy density and power capability over the entire SOC window because of the low impedance of LFP at low SOC range.

The blended cathodes are a very attractive combination of material that can be used to achieve a better performance than the parent cathode material, with respect to certain operation requirements.

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