Short-range contacts govern the performance of industry-relevant battery cathodes

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HIGHLIGHTS

- Investigate impact of dry-mixing on industrially relevant secondary electrodes.
- Trends in slurry rheology predict trends in electronic conductivity.
- Electronic conductivity and rheology do not predict rate capability.
- Improving short-range electron contacts has the greatest impact on rate capability.

ABSTRACT

Fundamental understanding of how processing affects composite battery electrode structure and performance is still lacking, especially for industry-relevant electrodes with low fractions of inactive material. This work combines rheology, electronic conductivity measurements, and battery rate capability tests to prove that short-range electronic contacts are more important to cathode rate capability than either ion transport or long-range electronic conductivity. $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$, carbon black, and polyvinylidene difluoride in 1-methyl-2-pyrrolidinone represent a typical commercial electrode with < 5.5 wt% inactive material. Dry-mixing carbon black with active material decreases the relative fraction of bulk (free) carbon, as shown by small angle oscillatory shear and microscopy. More free carbon leads to a stronger gel network (more long-range particle contacts) and higher electronic conductivity of the dried films. Improvements in battery rate capability at constant electrode porosity do not correlate to electronic conductivity, but rather show an optimum fraction of free carbon. Simple comparison of rate capability in electrodes with increased total carbon loading (3 wt%) shows improvement for all fractions of free carbon. These results clearly indicate that ion transport cannot be limiting and highlight the critical importance of short-range electronic contacts for controlling battery performance.

1. Introduction

The lack of fundamental understanding of electrode processing on battery performance limits rational design of new processing techniques and commercial implementation of new materials. Current battery electrodes experience decreases in performance due to insufficient transport of electrons and ions to reaction sites within the electrodes. Gaining a fundamental understanding has been difficult due to disagreement in the field about whether ions or electrons are more limiting to electrode performance [1–20].

One school of thought has argued that rapid electron transport requires both long- and short-range electronic contacts [2,4,5,14,15]. Short-range contacts permit transport between active material particles, while long-range contacts permit rapid electron movement throughout

the whole electrode. An even coating of conductive additive on the surface of active material particles can drastically improve short-range electronic contacts [2,4]. Dominko et al. used gelatin to coat carbon black onto various active materials in the absence of binder and saw typical improvements 20 mA h/g at all C-rates for electrodes made with 2 wt% carbon black [14,15]. Bauer et al. used a high-speed dry mixer to coat carbon black onto active materials and found that dry mixing on its own was detrimental to performance. However, rate capability improved when a 4 wt% carbon coating and 10 wt% free graphite were combined [2]. Similarly, Bockholt et al. maintained the carbon content of cathodes at 6 wt% and varied the dry mixing intensity to find a maximum performance at intermediate intensities of dry mixing [4].

A contrasting school of thought has argued that tortuous ion pathways are the main limiting factor to battery performance. Inactive

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materials in the electrode can create tortuous pathways that slow down or completely block ion diffusion to sections of the electrodes [6,19,21]. This school of thought suggests that preventing porous conductive additive agglomeration and minimizing the amount of polymer binder will decrease the tortuosity of the ion pathways, making it easier for ions to diffuse though the electrode. Babinec et al. studied the mechanical and electrochemical impact of increasing the amount of polymer binder in $LiCoO_2$ cathodes without conductive additive. Increasing the binder concentration from 5 to 40 vol% decreased rate capability by 80% but had no effect on electronic conductivity, thus suggesting that ion transport was limiting [6]. Balke et al. studied intercalation of $LiCoO_2$ using electrochemical strain microscopy and atomic force microscopy and found that Li-ion diffusion greatly depends on grain boundaries. The authors proposed that improving ionic conductivity would overcome these grain boundary limitations [22]. Harris and coworkers studied the failure mechanisms of Li-ion battery electrodes through reconstruction and analysis of commercial electrodes, and emphasized the importance of ion transport in preventing electrode failure and improving electrode performance [19,20,23].

Despite disagreements in the literature, controlling the location and distribution of inactive material in the electrode is a common theme. Slurries are complex fluids, a well-studied classification of materials containing particles and polymer in solution. Complex fluids can form a variety of microstructures ranging from a fluid to a gel. Previous work from our group has studied the gelling mechanism that occurs in battery slurries. We have shown that in the case of micron-sized active material, only the concentration of free colloidal carbon black particles control the microstructure of the slurry [24]. Lee et al. generated electrode slurries with either a fluid or a gel microstructure by varying the mixing procedure [3]. The electrodes from the fluid microstructure had higher capacity retention over time and increased discharge capacity at higher discharge rates. The improvement was attributed to better homogeneity. Bauer et al. and Bockholt et al. found similar slurry microstructures, but argued that gel microstructures were more desirable than fluids due to the long-range conductivity that develops in a gel [2,4,5].

Informally, it is well known among academic battery researchers that high carbon concentrations are necessary for realizing the theoretical capacity of many materials. Academic battery formulations therefore typically contain 5-20 wt% conductive additive. The requirement of such high carbon concentrations suggests that for most electrodes, electron transport is more limiting than ion transport. However, commercial high-energy-density electrodes require the minimization of inactive species like conductive additive and polymer binder. In order to resolve these contradictions and understand the factors limiting Li-ion battery performance, this work studies the impact of total carbon black concentration and free carbon black concentration on the rheology, electronic conductivity and electrode rate capability. $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ with carbon black concentrations of 2.5 and 3.0 wt% carbon black in the presence of polyvinylidene difluoride was chosen as a representative commercial formulation [25,26]. Our work therefore consolidates previous literature observations in the context of relevant commercial concentrations.

2. Materials and methods

2.1. Electrode composition and processing

Electrodes were composed of $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ (NMC) (Toda America, NM3100) with a mean particle size of 10 μm and a BET of 0.5 m^2/g as the active material, carbon black (CB) (MTI, Super C65) with a BET 62.6 m^2/g as the conductive additive, and polyvinylidene difluoride (PVDF) (Arkema, MW = 380k) as the polymer binder. The slurry was processed using 1-Methyl-2-pyrrolidinone (NMP) (Sigma-Aldrich, ≥99%) as the solvent. Two electrode compositions were tested: (1) 95 wt% NMC, 2.5 wt% CB, 2.5 wt% PVDF; (2) 94.5 wt%
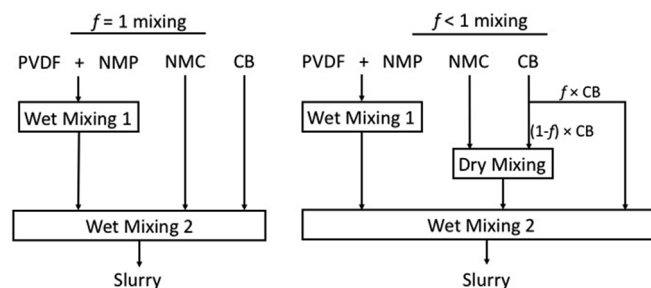

Fig. 1. Flow cart illustrating mixing procedures with varying f, fraction of free CB.

NMC, 3.0 wt% CB, 2.5 wt% PVDF. During processing the polymer concentration in solvent was maintained at 48 mg/mL, and the mass ratio of active material and polymer was maintained at 38:1.

Fig. 1 features a flow diagram of the two types of slurry preparation processes used in this work. The total CB concentrations tested in this paper were 2.5 wt% and 3.0 wt%. A fraction of the total CB $(1 − f)$ was used in the dry mixing and a fraction f of the CB was withheld from dry mixing and designated as "free". Slurries with $f = 0$, 0.25, 0.5, 0.75, and 1 were tested. NMC and CB were mixed in a ball mill (Tumbler's Tumbler, Model AR-2) with an aluminum canister, 20 g of material, and 1 stainless steel ball per gram of material for 16 h. The ratio of NMC to CB in the ball mill was dependent on the f value, as can be seen in Fig. 1. Because dry mixing does not always result in complete adhesion between NMC and CB, f represents a lower limit for the fraction of free carbon. Slurries were mixed by first dissolving PVDF fully into NMP in a Thinky planetary mixer at 1800 rpm. After the PVDF was mixed into the NMP, NMC and CB were added and mixed for 7.5 min in the planetary mixer at 1800 rpm.

After the slurry was mixed, it was coated onto an aluminum current collector (20 μm in thickness) using a doctor blade set to 100 μm and an automatic coater (TOB Energy). The shear rate applied during coating was calculated from video recording to be 200–300 1/s. The coating dried overnight at room temperature, and was then vacuum dried at 120C for 12 h. Once the drying process was completed, multiple 3/8″ diameter electrodes were punched from the film. Electrodes were calendered individually with a Carver melt press at 20 MPa of pressure. Before they were cycled into an Ar atmosphere glovebox (LC Technology Solutions), the electrodes were heated for 1 h at 100C to ensure no water was present. Once the electrodes were cycled into the glovebox, they were assembled into 2032 sized coin cells with a ½″ diameter lithium metal counter electrode, LP30 electrolyte and two Celgard separators.

Following the procedure of Peterson et al., a nonconductive substrate was used to measure the in-plane electronic conductivity of the final dried films without interference from the Al substrate [16]. Our modification eliminated the delamination step by coating directly onto glass. The glass microscope sides were secured and cleaned with isopropanol, and coated using the automatic coater. Identical protocols were maintained for battery electrodes and conductivity samples. After the slurry was dried, the individual microscope slides were removed from the aluminum foil and then cut into four 1.5″ x 0.5″ samples using a glass cutter.

2.2. Characterization

Rate capability tests were performed using an Arbin battery cycler. First, the batteries were charged and discharged at C/10 between 4.3 and 3 V for four cycles. The following cycles were all charged at C/10 and discharged at C/2, 1C, 2C, 5C, 10C, and then C/2 again for four cycles each. Electronic conductivity tests were performed using a Bio-Logic potentistat and a four-line probe based on the design and technique developed by Peterson [16]. The samples were secured on the