

High-molecular-weight polyvinylidene difluoride binder for high-capacity cathodes

Maurizio Biso, Md-Jamal Uddin, and Sung-Jin Cho

Slurries prepared with optimized binders exhibit good rheological characteristics and are a cost-effective option for lithium-ion battery applications.

Lithium-ion batteries (LIBs)—the most promising energy storage technology currently available—enable a wide range of applications, including hybrid electric vehicles and electric vehicles.¹ For these particular applications, the main requirements for the LIBs are a high energy density and fast charging/discharging capabilities. To further improve the energy density of LIB cells, it is thought that two simple approaches can be pursued. In the first of these approaches, a high-energy cathode material, e.g., a nickel-rich nickel manganese cobalt (Ni-rich NMC) material,^{2–4} is used. Such materials are considered a key factor for achieving the next generation of Ni-rich cathodes.⁵ In the second approach to improving the energy density of LIB cells, larger amounts of the active material are added to the cell. This means that it is necessary to correspondingly reduce the content of the inactive materials (i.e., the binder and conductive carbon in the electrode).

The Ni-rich NMC material $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$ (where Li is lithium and O is oxygen) has strong electrochemical performance characteristics—i.e., high voltage operation, very good specific capacity, and reasonable costs for general consumer applications^{6–10}—and is thus particularly suitable for use in LIBs. In addition, polyvinylidene difluoride (PVDF) is widely recognized as the best performing LIB binder. This material exhibits excellent chemical and electrochemical resistance, as well as remarkable adhesion and cohesion properties. However, to reduce the amount of PVDF in LIBs (and thus increase the amount of the active material), it is necessary to understand how these high-molecular-weight (high-MW) binders behave chemically and electrochemically in Ni-rich NMC materials.

The purpose of our study¹¹ was to understand how various high-MW PVDF binders interact with a Ni-rich NMC cathode material and to thus identify the best electrode formulation for high-energy cell fabrication. Specifically, we have studied the rheological behavior of



Figure 1. Photographs of the slurries (about 20mm in diameter) prepared with different polyvinylidene difluoride (PVDF) binders. (a) Slurry produced by emulsion polymerization with Solvay Solef 5130 (molecular weight, MW, >900,000). (b) PVDF-A slurry (MW>900,000) produced by emulsion polymerization. (c) PVDF-B slurry (MW>1,000,000) produced by suspension polymerization.

high-capacity Li-rich and Ni-rich NMC slurries so that we can establish an optimized high-MW PVDF. For our study we chose three commercial-grade PVDF binders (manufactured by different polymerization methods) that are specifically recommended for application in LIBs. The first of these binders—Solvay Solef[®] 5130—has a high MW (MW>900,000) and is produced by suspension polymerization. We also used a binder produced by emulsion polymerization, with MW>900,000 (PVDF-A), and one manufactured by suspension polymerization (PVDF-B) that has MW>1,000,000.

In our work we followed a standard mixing procedure to prepare slurries with the three different PVDF binders. To achieve good coating with this process, it is important to obtain homogeneous and stable dispersion of the active and inactive components in the solvent.^{12–15} This dispersion must be homogeneous for all the components even though solid particles in slurry tend to have different sizes. For instance, active material particles are usually a few micrometers in size, whereas carbon black particles are significantly smaller (less than 100nm). Moreover, the active material slurry must be stable over a range of storage times

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(hours to a few days) so that they are compatible with industrial process timelines.

We conducted rheological tests on our prepared slurries to compare their colloidal stabilities. We observed irreversible gelation after a few days for the PVDF-A slurry. We attribute this to its small particle size, which is a result of the emulsion polymerization. In contrast, the PVDF-B slurry changed irreversibly during the first few days. We observed this gelation as the formation of aggregated patches that cannot be redispersed even after prolonged mixing. To our surprise, we did not observe any gelation, even after 20 days, for the Solef 5130 slurry. The gelation of the three slurries is illustrated by the photographs in Figure 1.

We also used charge–discharge cycling and electrochemical impedance spectroscopy (in a coin cell configuration) to characterize the electrochemical nature of our materials. We obtained good adhesion for the Solef 5130 slurry, both for a formulation with a 2% binder content and for a formulation with half the binder quantity (i.e., 1%). By halving the amount of binder, we increased the loading of the active materials in the formulation and thus improved the volumetric and gravimetric energy density of the material. Furthermore, by using less of the binder in the formulation, we produced a lower charge transfer resistance and enabled a greater power density. Our results (see Figure 2) indicate that the capacity retention at a high charge rate (i.e., higher power density) starts to improve from a discharge rate of 2C. At this rate, the slurry formulation containing 1% Solef 5130 has a specific capacity of 159mAh/g, whereas the other slurries have values of 156mAh/g. The specific capacity for the 1% Solef 5130 slurry at a discharge rate of

4C is 152mAh/g, and 148mAh/g for the slurries prepared with other binders.

In summary, we have investigated the interaction between high-MW PVDF binders (prepared by different polymerization methods) and Ni-rich NMC cathode materials. The rheological behavior of the slurries provides evidence that the binder preparation method has a strong effect on the slurry stability. In particular, we observed that a slurry prepared with suspension polymerized Solef 5130 PVDF is very stable and can be stored for more than a month. We have also conducted electrochemical tests on coin cells that demonstrated the equivalent performance of all our slurry formulations (even for the formulation containing only 1% Solef 5130). By using a smaller amount of the binder material, the active material loading in the electrode can be increased and give rise to a greater energy density for many LIB applications. In the next stage of our research we will design and investigate a waterborne PVDF high-MW binder with a high-capacity cathode material for automotive applications. Specifically, we will incorporate the aqueous high-MW PVDF binder and characterize its physical (mechanical), chemical, and electrochemical performance to assess whether it can meet the next-generation automotive battery goals (i.e., in terms of low cost, and long durability and performance).

Author Information

Maurizio Bisio

Solvay Specialty Polymers
Bollate, Italy

Maurizio Bisio is a senior researcher in the Lithium-Ion Battery team. He has a master's degree in industrial chemistry (University of Bologna, Italy) and an engineering PhD from the Italian Institute of Technology of Genoa. He has more than 10 years of experience working on a wide range of electrochemical devices, including lithium-ion batteries, supercapacitors, direct methanol fuel cells, and electrochemical actuators.

Md-Jamal Uddin and Sung-Jin Cho

North Carolina Agricultural and Technical State University
Greensboro, NC

Md-Jamal Uddin is currently a PhD student in the Joint School of Nanoscience and Nanoengineering.

Sung-Jin Cho is an assistant professor in the Joint School of Nanoscience and Nanoengineering, and he has served as the director of

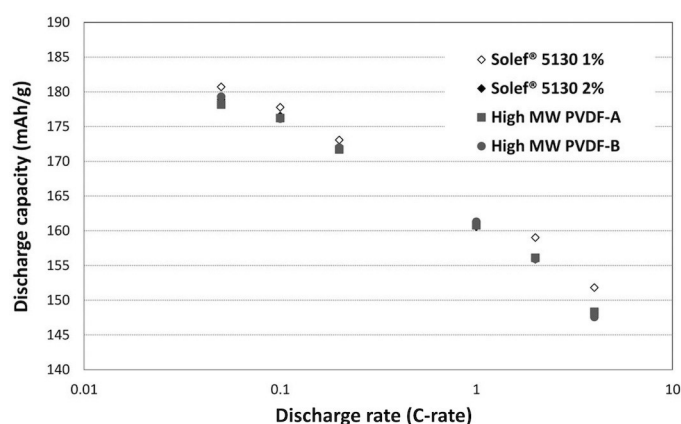


Figure 2. Discharge capacity of slurries as a function of discharge rate (at discharge rates of 1C and 4C a cell will discharge in one hour and in a quarter of an hour, respectively). Results are provided for different formulations of the PVDF binder in the cathode, including two Solef 5130 formulations (which include 1 and 2% of the binder).

the Nano Energy Laboratory since August 2014. From 2008 to 2014, he worked as a technical lead at Johnson Controls Battery Technology Center in Milwaukee. He also led the US Advanced Battery Consortium program to design and evaluate battery material and lithium-ion cell engineering for automotive applications for more than six years. He has been working on lithium-ion batteries since 1998 in Korea and held multiple positions at LG before beginning his PhD in the United States.

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