



Short communication

## Cross-linkable urethane acrylate oligomers as binders for lithium-ion battery

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## ABSTRACT

Cross-linked polymers generated from low molecular weight oligomers were investigated for the first time as electrode binders in lithium-ion batteries. With urethane acrylate-based binder precursors, electrode laminates of  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  (NMC) with good physical properties were prepared via a thermally initiated free-radical polymerization process. The cured NMC electrode was evaluated in both NMC/Li and NMC/MCMB cells and showed excellent cycling performance and C-rate capability.

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### 1. Introduction

Polymer binder is one of the essential components of the composite electrode in lithium-ion batteries [1]. In the past decade, the demand for next-generation lithium-ion batteries has aroused intense interest in search of advanced energy storage materials, wherein a diversity of polymers have been investigated as binders for various electrode materials [2–9]. Although binders are considered as one of the inactive components in a lithium-ion cell, their chemical and physical properties are found to be closely related to the electrochemical performance of the entire battery [10–12]. Evidently, there has been increasing attention to the development of polymer binders that are tailored to meet specific needs [13–17].

In commercial and the state-of-the-art lithium-ion batteries, most binder materials are based on electrochemically inert, high molecular weight polymers. Under certain circumstances, these polymers are structurally modified with functional groups to improve adhesion and binder-particle interaction [14,15,17]. Such chemical modifications either require incorporation of functional monomers during polymer synthesis or post-polymerization functionalization, both posing nontrivial synthetic challenges to the development of functional polymer binders. Chemically cross-linked polymers have been demonstrated to improve battery performance, which was attributed to the increased mechanical stability of the electrode during cycling [18,19]. However, these examples were still based on high molecular weight polymers that underwent cross-linking upon treatment. In contrast, a general method using low molecular weight, reactive oligomers that can be cross-linked in-situ during electrode preparation has yet to be established. One of the

advantages of this approach is that it would benefit from a much broader selection of functional, reactive oligomers, which allows for systematic studies on the correlation between the binder properties and the electrochemical performance of the electrode.

Acrylate oligomers have been widely used in the coating industry due to their high reactivity and structural diversity [20]. Among a wide range of commercially available acrylate oligomers, urethane acrylates provide good adhesion, flexibility, and chemical resistance that are desired properties for binder materials. We report herein the preparation and cycling performance evaluation of the composite cathode fabricated with thermally cross-linkable, urethane acrylate-based binders.

### 2. Experimental

#### 2.1. Materials

Aliphatic urethane acrylate oligomers (UA, GENOMER\* 4267), aromatic urethane acrylate oligomers (AUA, GENOMER\* 4217) and methacrylated phosphate ester (MPE, GENORAD\* 40) were acquired from RAHN USA. 1,6-Hexanediol diacrylate (HDDA), isobornyl acrylate (IBA), 2,2'-azobis(2-methylpropionitrile) (AIBN), 4-methoxyphenol, toluene, isopropanol, and dimethyl carbonate (DMC) were purchased from Sigma-Aldrich and used as received without further purification.

#### 2.2. Solvent swelling test of cured polymers

The oligomers and AIBN (1 wt%) were mixed thoroughly in a PTFE beaker and then transferred to a preheated (80 °C) oven in an Ar-filled glovebox for 1–4 h to complete curing. The cured polymer

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was weighed and submerged in DMC for 48 h, after which the percentage of weight gain was recorded.

### 2.3. Preparation of thermally cured electrode

$\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  (NMC) (85 wt%), Super P Li (5 wt%), and oligomer mix (10 wt%, composed of 9.5 wt% oligomers/monomers and 0.5 wt% AIBN) were thoroughly mixed in toluene or isopropanol by magnetic stirring or in a planetary centrifugal mixer. The resulting slurry was cast into a 40- to 80- $\mu\text{m}$  laminate with doctor blade on an Al current collector (15  $\mu\text{m}$  in thickness), which was placed in a fume hood for a few minutes to remove solvent and then cured in an Ar-filled glovebox at 80 °C for 16 h. The cured electrode laminate was calendared to desired porosity (~35%) and punched into disks of 1.6  $\text{cm}^2$  with an active material loading of 5–9  $\text{mg}/\text{cm}^2$ . The punched electrodes were further dried at 80 °C in a vacuum oven

and used for coin cell testing. For comparison, conventional PVdF binder was used to prepare the baseline electrodes.

### 2.4. NMR study on electrode curing process

The NMC electrode laminates were prepared according to the aforementioned curing procedure. During the curing process, samples were removed from the glovebox at certain time intervals. The electrode material was scraped off the Al current collector, weighed, and then suspended in  $\text{CDCl}_3$  containing 0.2 wt% 4-methoxyphenol as an internal standard for 24 h. The amount of uncured components was then analyzed by a Bruker DMX 500 NMR spectrometer. The degree of cross-linking (0% for the pristine, uncured sample) was estimated by calculating the integration ratio of the acrylate protons versus the aromatic protons of 4-methoxyphenol.

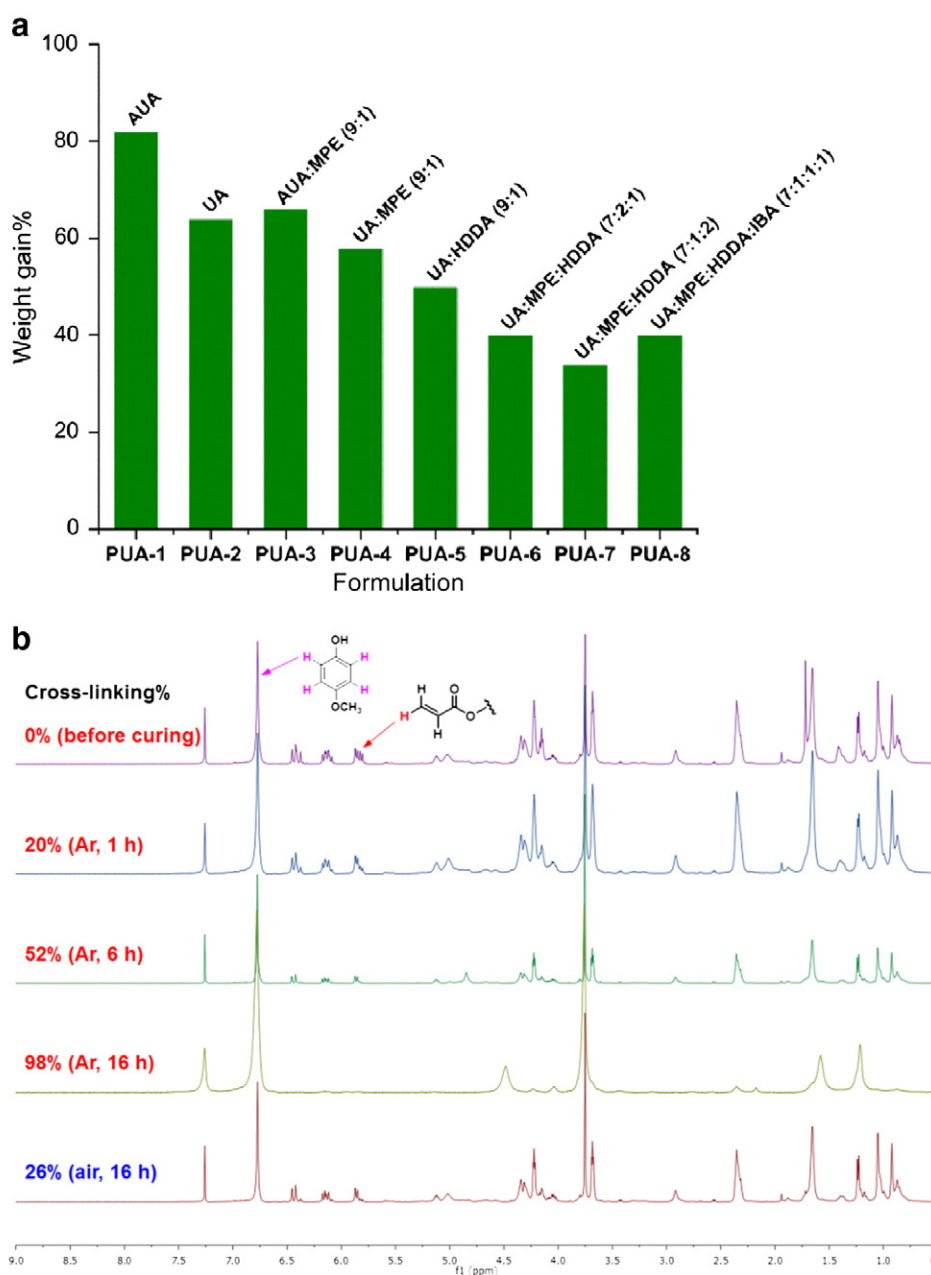


Fig. 1. (a) Solvent swelling test of cured polymers. (b) NMC electrode laminate curing process at 80 °C monitored by  $^1\text{H}$  NMR spectroscopy.

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