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Evaluation of guar gum-based biopolymers as binders for lithium-ion batteries electrodes

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ABSTRACT

Herein we report the investigation on the use of guar gum and two of its derivatives as LIB positive electrodes binders. These polymers are electrochemically stable within the operating voltage of LIBs (0.01–5 V vs Li/Li^+) and do not show evidence of thermal decomposition up to 200 °C. The electrochemical performance of lithium nickel manganese cobalt oxide (NMC) electrodes made using guar gum is excellent as indicated, for instance, by the delivered capacity of 100 mAh g^{-1} upon 5C rate cycling. X-ray Photoelectron Spectroscopy (XPS) measurements of pristine electrodes reveal as the binder layer surrounding the active material particles is thin, resulting in the above-mentioned electrochemical performance. Full lithium-ion cells, utilizing guar gum on both positive and negative electrodes, display a stable discharge capacity of ~110 mAh g^{-1} (based on cathode active material) with high coulombic efficiencies. Post-mortem investigation by XPS of cycled graphite electrodes from full lithium-ion cells revealed the formation of a thin solid electrolyte interface (SEI).

1. Introduction

Since their introduction in 1991, lithium-ion batteries (LIBs) are employed as power sources in a large variety of portable devices. Moreover, the range of applications for which LIBs are used or considered suitable is continuously growing due to their higher power and energy densities compared to other secondary batteries chemistries, such as lead-acid and nickel metal hydride (NiMH) [1].

In small electric devices batteries are used to enable wireless use, while in hybrid and electric vehicles batteries are employed, respectively, as a secondary or main power supply, offering higher energy efficiency and lower CO_2 emissions in comparison with a standard internal combustion engine (ICE). Boosted by the urgent need to reduce the dependency on fossil fuels and, especially, lowering the environmental impact, the automotive industry has been given great efforts to introduce LIBs in electric vehicles [1–3].

Nevertheless, the development of LIBs technology is still facing several issues, among which the improvement of safety and the reduction of costs play a major role. Recently, a detailed analysis of the costs associated with the different steps of battery production has been reported [4], from which the electrodes preparation and processing emerge among the main factors affecting the battery cost. An electrode layer consists of three main components: active material, conductive carbon and binder. The binder is an electrochemical inactive component that has the function to provide the adhesion between active material, conductive carbon particles and the current collector. Therefore, binders are key components affecting the rheological, mechanical and electric properties of the electrodes and, at the end, the cell performance [5].

The state-of-the-art in the anodes production, i.e., graphite, is represented by the mixture of two binders, sodium carboxymethyl cellulose (NaCMC) and styrene butadiene rubber (SBR). This combination is very reliable and offers the advantage of being water-based. On the other hand, cathode tapes are still made using poly (vinylidene difluoride) (PVdF) as binder, which is considerably more expensive ($ ~17 kg) than NaCMC ($ ~1 kg) [4]. Moreover, PVdF requires the use of N-methyl-2-pyrrolidone (NMP), a highly volatile toxic solvent, which has to be recovered during the electrode drying step. It is clear that switching to aqueous process also

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for the positive electrode, permits to decrease the environmental impact and the cost associated with Li-ion battery production [6]. As reported by Xu and co-workers [7], lithium nickel manganese cobalt oxide (NMC) electrodes prepared using NaCMC display enhanced rate capability respect to PVdF-based electrodes. Superior cycling stability were also reported for $LiNi_{0.5}Mn_{1.5}O_4$ [8] and $LiNi_{0.4}Mn_{0.4}Co_{0.2}O_2$ (NMC-442) [9] electrodes using NaCMC instead of PVdF. However, the aqueous processing of oxide-based cathode materials is still a challenge [10]. Indeed, it requires that the active material is stable in contact with water, i.e., without incurring in detrimental reactions such as lithium leaching. Moreover, the aqueous slurries of metal oxides display high pH values (>11) leading to the corrosion of the aluminium current collector during the electrode casting and drying. This specific issue has been deeply investigated by our and other research groups. Different approaches have been explored to enable aqueous processing for cathodes, such as the use of a protecting carbon layer on current collector [11,12], the combination of NaCMC and urethanes polymers [13], and the reduction of the slurry's pH by addition of mild acids [14]. In particular, the last solution is simple and easy to be introduced in the already established electrode production lines.

Many different synthetic and natural polymers have been considered as binders for aqueous electrode processing. Cuesta et al. [15] investigated the influence of several natural polysaccharides in graphite-based anodes. Natural polymers, as guar gum and lotus bean gum, were also applied to silicon-based electrodes in order to support the undesired, but occurring silicon volume changes during the electrochemical reactions [16–18]. In our previous work, we reported the use of bio-source polymers as binder in lithium titanate (LTO) electrodes, such as NaCMC, guar gum and pectin [19]. In line with Kim et al. [20], improved electrode's rate capability can be achieved using guar gum instead of NaCMC. Zhang et al. [21] reported superior cycling stability of lithium-rich cathode by using guar gum as binder, while Lu et al. [22] reported improved capacity retention using guar gum in lithium-sulphur cells. The superior electrochemical performance achieved by the electrodes containing guar gum has been attributed to the higher affinity of this polymer toward the non-aqueous electrolyte with respect to NaCMC. Moreover, as reported by other authors [17,23] guar gum coordinates Li^+ similarly to polyethylene oxide (PEO) in solid polymer electrolytes, leading to enhanced ionic conduction. However, no much attention has been given to guar gum derivatives obtained by the modification of the hydroxyl groups. We previously reported on the use of hydroxypropyl guar gum in combination of SiO_2 to prepare a porous membrane and its application as LIBs separator [24]. Herein we study natural guar gum and two derivatives, namely, hydroxypropylated guar gum (HPG) and guar hydroxypropyltrimonium chloride (HPTG), as binders for lithium nickel manganese oxide $Li\ [Ni_{0.33}Mn_{0.33}Co_{0.33}]O_2$ cathode. The biopolymers are examined in terms of thermal and chemical stabilities. The electrode morphology and electrochemical behaviour are evaluated and compared with those of NaCMC based electrodes. Finally, the investigation on Li-ion cells comprising both electrodes prepared via aqueous processing is presented, coupled with the post-mortem analysis by X-ray Photoelectron Spectroscopy (XPS).

2. Experimental

2.1. Thermal and electrochemical stability evaluation

The thermogravimetric analysis (TGA) experiments were carried out on a Q5000 IR TGA instrument (TA Instruments, USA) by heating the samples in open aluminum pans from 30 °C up to 600 °C with a heating rate of 5 °C min^{-1} under a nitrogen gas flow (25 mL min^{-1}). The samples (10–20 mg) were subjected to the test without any pre-treatment.

Binder films were casted on aluminium foil in order to evaluate their electrochemical stability within the cathode operational potential range. Three-electrode Swagelok® cells were assembled using 1 M solution of lithium hexafluorophosphate ($LiPF_6$) in a mixture of ethylene carbonate and dimethyl carbonate (EC:DMC (1:1 w/w)) (LP30, BASF, Germany) as the electrolyte (supported on the glass fiber membrane GF/D from Whatman) and Li metal as quasi-reference electrode and counter electrode. The cyclic voltammetry measurements were performed using a VMP3 (BioLogic) between 2.5 and 5 V with a scan rate of 0.5 mV.

2.2. Electrode preparation

Electrodes were prepared using as the binder either NaCMC (CRT 30000 PA 09 (anode) and CRT 2000 PPA 12 (cathode), Walocel, Dow Wolff Cellulosics, Germany) or natural guar gum (GG), hydroxypropylated guar (HPG), and hydroxypropyltrimonium chloride guar (HPTG) (all from Lamberti SpA, Italy).

For the graphite electrodes, styrene butadiene rubber (SBR, TRD 102A, JSR Micro, USA) was added to improve the flexibility of the coated material layer. $Li\ [Ni_{0.33}Mn_{0.33}Co_{0.33}]O_2$ (NMC; average particle size $d_{90} = 10\ \mu m$, TODA, USA) was used as cathode material. The conductive carbon was C-NERGY Super C45 (Imerys, Switzerland). Details of the electrodes compositions are given in Table 1.

NMC electrodes were prepared as it follows. After dissolving the binder in water, the conductive carbon was added and the mixture was stirred for at least 6 h. To the homogenous dispersion, the active material and phosphoric acid (1 wt.% with respect to the weight of the active material, Bernd Kraft GmbH, Germany) were added to the slurry, which was stirred for 2 more hours. The addition of PA was performed to prevent the corrosion of aluminium current collector according to previously published results [14,19,25]. The same procedure was used for the graphite electrodes, however, SBR (2 wt.%) rather than phosphoric acid was added prior coating.

Finally, the slurries were mechanically mixed at medium-speed (5000 rpm) (4000-4/65, DREMEL, USA) prior casting either on copper (anode) or aluminium (cathode) foils. The coated electrodes were dried in an open atmosphere oven at 80 °C and, afterwards, under vacuum at 160 °C for at least 6 h. Prior to the electrochemical tests, small discs ($area = 1.13\ cm^2$) were punched out of the electrodes tapes and pressed using a manual press (Atlas manual hydraulic press 15T, Specac, UK) in order to reduce the electrode porosity, ensure a homogeneous surface and enhance electrode adhesion and density (anodes: 1 t cm^{-2}; cathodes: 10 t cm^{-2}).

2.3. Cell assembly and electrochemical tests

NMC electrodes were tested versus Li metal using pouch-bag cells. The cells were assembled in a dry room (R.H. <0.01% at 20 °C ± 1 °C) using 1 M solution of lithium hexafluorophosphate ($LiPF_6$) in a mixture of ethylene carbonate and dimethyl carbonate (EC:DMC (1:1 w/w)) (LP30, BASF, Germany) as electrolyte and the porous polyethylene membrane (Asahi Kasei, Hipore SV718, Japan) as separator. Full cells were assembled in three-electrode configuration (Swagelok®) using NMC and graphite electrodes with either NaCMC or GG as the main binder. 1 M of $LiPF_6$ in EC:DMC (1:1 w/w) with 1 wt.% VC was used as electrolyte, and the Whatman GF/D membrane as separator. Li metal was used as quasi-reference electrode.

The galvanostatic investigation of all cells was carried out at a constant temperature of 20 °C ± 0.1 °C (Binder KB 400) using a