



Hydrocolloids as binders for graphite anodes of lithium-ion batteries



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ABSTRACT

A series of seven different hydrocolloids are tested as water-soluble binders for synthetic graphite (SG)-based electrodes of lithium-ion batteries (LIBs) and compared with the standard poly(vinylidene difluoride) (PVDF) binder. The hydrocolloids selected are sodium carboxymethyl cellulose (Na-CMC), sodium alginate (Na-Alg), gum arabic (GA), xanthan gum (XG), guar gum (GG), agar-agar (AA) and carrageenan (CAR), the latter three with no precedents in the literature. They all show thermal and electrochemical stability under the experimental conditions employed. For SG/hydrocolloid electrodes, binder concentrations of 5 wt% are found to be optimal, providing outstanding electrochemical performances for electrodes with Na-Alg Na-CMC, XG and GG in galvanostatic cycling experiments at constant ($C/10$, with $C = 372 \text{ mA g}^{-1}$) and variable (from $C/10$ to $2C$) current rates, which are comparable, or even superior to those of SG/PVDF electrodes with higher binder content (8 wt%). In contrast, SG/GA, SG/CAR and SG/AA electrodes show poorer electrochemical performances, most likely owing to the low adhesion capacity of the binder (GA and CAR), or the formation of films covering the SG particles (CAR and AA).

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1. Introduction

Binders play a key role in the electrodes of Li-ion batteries (LIBs). Typically, they consist of polymers or polymer mixtures which (i) hold the active materials particles and conductive additives together, (ii) are electrochemically stable in the operational potential range of the battery (0–5 V), (iii) are elastic and/or able to withstand significant volume changes and (iv) provide adhesion to the electric current collectors. Among them, poly(vinylidene difluoride) (PVDF) complies with all the requirements and has been the binder of choice for most of the commercial LIBs since their introduction in the global market in 1991, both in carbon-based anodes and layered metal oxide cathodes [1,2]. However, the use of PVDF has some major drawbacks as well, the most important being the need to use a toxic organic solvent, N-methyl-2-pyrrolidone (NMP), to form slurries with the active materials and additives to cast the electrode formulation. Additionally, focusing on graphite-based anodes, there are some safety concerns due to exothermic formation of F-containing species at high temperatures by reaction of PVDF with LiC_6 , which may trigger the onset of thermal runaway [3,4].

Therefore, the search for fluorine-free, “greener” and safer binders to replace PVDF has been an intensive area of research in

the last years. Among them, water-soluble polymers have been successfully used for both anode and cathode formulations [1]. Moreover, in the case of Si-based anodes, where the volume increase by lithiation is up to 400% and PVDF proved not to be an effective binder in terms of cycling stability, the use of water-processed polymeric binders such as polyacrylic acid (PAA) [5] and its sodium salt (Na-PAA) [6,7], combinations of sodium carboxymethyl cellulose (Na-CMC) with [8,9] or without [7–15] styrene-butadiene rubber (SBR), sodium alginate (Na-Alg) [16] or carboxymethyl chitosan [17] provided superior cycle performance. Interestingly, three of the latter binders, namely Na-CMC, Na-Alg and carboxymethyl chitosan, belong to a family of bio-derived water-soluble and environmentally friendly polymers known as hydrocolloids, which encompass a wide range of polysaccharides and proteins traditionally used in different industrial sectors, especially food industry, to perform a number of functions including thickening and gelling aqueous solutions, stabilizing foams, emulsions and dispersions [18]. In addition to this, they are usually more cost-effective than PVDF (e.g., 1–2\$/Kg Na-CMC vs 15–18\$/Kg PVDF [15]).

Focusing on the utilization of hydrocolloids in graphite anodes, there are some examples in the literature which include: gelatin [19–24], Na-CMC [9,12,15,24–28], Li-CMC [29], Na-Alg [16], xanthan gum (XG) [29] or chitosan [30]. The electrochemical results obtained are comparable, and sometimes even superior, to those of PVDF-based anodes in terms of cyclability, rate capability and irreversible capacity in the first discharge-charge cycle, and in

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addition, lesser amount of the hydrocolloid was generally required to prepare suitable anodes. On the basis of these results and considering that the use of water instead of organic solvents for the electrode manufacturing involves lower costs and also reduces the associated environmental risks, hydrocolloids are a solid alternative as binders for commercial LIBs. In fact, graphite-based anodes of some of these batteries are being already produced using combinations of Na-CMC with the synthetic rubber SBR [31]. However, the implementation of these natural, cheap and environmental friendly binders still requires further research as regards origin, composition and properties to optimize the electrode preparation and electrochemical performance.

With these precedents in mind, in this paper different hydrocolloids are investigated as potential alternative binders to PVDF for anodes of LIBs containing synthetic graphite (SG) as active material. The following three groups of hydrocolloids were selected: agar-agar (AA), carrageenan (CAR) and guar gum (GG) which, to the best of our knowledge, have not been used for this application previously, xanthan gum (XG), sodium alginate (Na-Alg) and sodium carboxymethyl cellulose (Na-CMC) which, as mentioned above, have already been studied as graphite binders, particularly the latter one, and finally, gum arabic (GA), which has been only documented in a patent [32]. In the first place, thermogravimetric and voltammetric analyses were performed for these binders to assess their thermal and electrochemical stabilities in the range of temperatures and potentials in which LIBs operate. Afterwards, the amount of hydrocolloid binder in the electrodes was optimized and the galvanostatic cycling behavior vs Li was tested at constant and variable current rates. Finally, the results were compared with those of the PVDF-based electrodes.

2. Experimental

2.1. Materials: source and characterization

Synthetic graphite (SG) TIMREX SLP50 provided by TIMCAL Spain (www.timcal.com) was used as the active material in the working electrodes. According to the supplier, this is a highly pure graphite (ash content < 0.10 wt%) with a perfect crystalline structure (interplanar distance 0.3354–0.3356 nm, crystallite size $L_c > 250$ nm) and a Potato[®]Shape particle morphology that is commercialized as active material for negative electrodes of lithium-ion batteries. Seven commercially available hydrocolloids were selected as binders: Na-CMC (Mw ~ 700,000, degree of substitution 0.80–0.95), GA from acacia tree and CAR, suitable for gel preparation, supplied by SIGMA-ALDRICH; Na-Alg, AA, GG and XG provided by INDUSTRIAS ROKO (www.rokoagar.com). These products are pure polysaccharides, except AA and GA that are, respectively, a mixture of two polysaccharides of high (agarose) and low (agaropectin) molecular weights and a complex mixture of oligosaccharides, polysaccharides and glycoproteins [18]. For comparative purposes, PVDF from SIGMA-ALDRICH was also utilized as binder. The molecular structure of all the polymeric binders can be seen in the Supporting Information (Fig. S1).

Thermogravimetric analyses (TGA) of the binders were performed in a TGA Q5000IR analyzer from TA instruments to study their thermal stability. The samples were placed in platinum pans and heated at 5°C min^{-1} up to 600°C in an air flow (100 mL min^{-1}).

2.2. Cell preparation and electrochemical measurements

Two-electrode (working + counter) Swagelok-type laboratory cells were used for the electrochemical characterization of both binders themselves (binder electrode) and SG in the presence of the different binders (SG/binder electrode). The

working SG/binder electrodes were prepared by mixing and vigorously stirring SG (98–88 wt%) and the corresponding hydrocolloid binder (2–12 wt%) aqueous solution at a concentration of ca. 0.3 wt%. The binder solutions were prepared at room temperature except for AA that was heated to the boiling point of water in order to achieve complete dissolution. A few drops of the resultant slurry were deposited onto a copper disc of 12 mm of diameter and $25\ \mu\text{m}$ of thickness and was then dried under vacuum at 120°C for 2 h. Finally, the electrode was hydraulically pressed at a pressure in the range of 9–90 MPa, and the load (active material + binder) was calculated by weight difference. As an exception, much lower pressure ($\ll 9$ MPa) was applied on the electrodes prepared with GA and CAR binders. The preparation of the electrodes using PVDF binder in 1-methyl-2-pyrrolidone (NMP) solution at a concentration of 1 wt% was analogous. The loadings in the electrodes were in the interval 1.77 – $10.62\ \text{mg cm}^{-2}$. For the preparation of the binder working electrodes, a few drops of an aqueous solution of the hydrocolloid or PVDF in NMP at a concentration of 1 wt% were spread over the copper discs followed by drying and pressuring in the conditions mentioned above. Binder loadings from 0.62 to $1.59\ \text{mg cm}^{-2}$ were calculated for these electrodes. In all cases, metallic lithium discs of 12 mm diameter were used as counter electrodes. The electrodes were separated by two micro-fiber glass discs impregnated with the electrolyte solution, 1 M LiPF₆ (EC:DEC, 1:1, w/w). The cell assembly was carried out in a dry box under argon atmosphere with oxygen and water contents below 0.1 ppm.

The electrochemical measurements of the cells (galvanostatic cycling and cyclic voltammetry) were conducted in a Biologic multichannel VMP2/Z potentiostat. The galvanostatic cycling of the SG/binder electrodes was carried out in the 2.1 – $0.003\ \text{V}$ potential range versus Li/Li⁺ using constant (50 cycles at C/10, C = $372\ \text{mA g}^{-1}$) or variable (10 cycles at C/10, C/5, C/2, C, 2 C and back to C/10.) rates. The cyclic voltammograms of the binder electrodes were collected at a scan rate of $0.5\ \text{mV s}^{-1}$ for 10 cycles in the 0 – $3\ \text{V}$ potential range versus Li/Li⁺. For comparison, the graphite-based electrode prepared with PVDF binder (SG/PVDF) and bare Cu discs were also subjected to cyclic voltammetry under the same experimental conditions.

The surface morphology of the SG/binder electrodes was analyzed with scanning electron microscopy (SEM) using a Zeiss DMS-942 microscope.

3. Results and discussion

3.1. Binders: thermal and electrochemical stability

The thermal stability of the binders was measured by TGA and the corresponding profiles of weight or derivative weight vs temperature are shown in Fig. 1. The hydrocolloids exhibit a weight loss in the range 7–13% below 150°C (Fig. 1a) with the maximum weight loss rate occurring at 50 – 60°C , as seen in the derivative thermograms (Fig. 1b). This certainly relates to desorption of water bound to the saccharide structure [33] and is in quite good agreement with the moisture content analysis provided by the commercial suppliers for the different hydrocolloids. More importantly, all of them proved to be thermally stable at least up to 200°C , which roughly corresponds to the onset temperature of the first decomposition stage for CAR and Na-Alg. The other hydrocolloids turned out to be slightly more stable with decomposition onset temperatures of ca. 220°C for XG and GG, 230°C for GA and 240°C for Na-CMC and AA. The present data fit well with those found in the literature for some of these and other related polysaccharide-based gums, which show decomposition stages starting above 200°C [29,33,34]. In all instances, additional decomposition stages can be observed up to 600°C leading to total

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