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New eco-friendly low-cost binders for Li-ion anodes

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Abstract In the production of commercial Li-ion batteries, the active materials slurries are generally prepared using polyvinylidene fluoride (PVdF) as binder because of its good adhesion properties and electrochemical stability. Unfortunately, there are some disadvantages related to the use of PVdF: the most important is the use of toxic and environmentally unfriendly solvents, such as *N*-methyl-pyrrolidone (NMP), and the second is the high costs. In the light of these considerations, it seemed straightforward to investigate the suitability of some water-soluble, inexpensive, and eco-friendly materials to test as alternative binders (sodium alginate, chitosan tragacanth gum, gelatin). The rheological properties of these materials have been investigated in addition to the electrochemical characterization. Furthermore, graphite electrodes with PVdF, carboxymethyl cellulose (CMC), and styrene-butadiene rubber (SBR) binders have been considered for sake of comparison. We found that some of these water-soluble binders, besides good electrochemical performances, showed a high adhesion to the current collector and a good electrochemical stability under the experimental conditions employed, which makes them interesting for the next generation of Li-ion batteries.

Keywords Li-ion batteries · Anode · Aqueous binder · Eco-friendly

Introduction

Lithium-ion batteries (LIBs) are to date the most performing among the rechargeable batteries in commerce, thanks to their high energy density, long cycle life, and good power capacity [1, 2], that makes LIBs suitable as energy storage devices and for EV or HEV [3].

Unfortunately, LIBs show some drawbacks, mainly related to cost and safety issues [4–6]. Most of the recent research activity has been focused on the characterization of new electrode active materials and new electrolytes [7]. Being a mature technology, it is not to be expected the discovery of new materials, increasing the LIB performance by tens of percentage. Improvements must be obtained taking into account all kinds of materials composing the whole system. The binder, present in the electrode material, is a so-called “inactive material” but it plays a key role in the formation of a stable active material network, ensuring the adhesion between the active material particles, the conductivity enhancer and the current collector [8]. In fact, if the binder does not have suitable properties, though present in the electrode for the 2–5% only, the performance and durability of the cell are compromised [7].

Since the introduction of the Li-ion battery in the market, PVdF has been the material of choice as electrode binder, thanks to its good electrochemical stability, binding capability, and its ability to absorb electrolyte for easy transport of lithium ions to the active material surface [9–14]. Unfortunately, PVdF is generally costly (15–18 euro/kg) [15], but even worse is the hazard connected to the environmentally unfriendly *N*-methyl-pyrrolidone (NMP) used as solvent in the process of electrodes

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preparation [16]. NMP is a heterocyclic compound, liquid at room temperature with a boiling point around 200 °C, it is part of the so-called volatile organic compounds (VOC), and is classified by the European Union as teratogen, toxic, and irritant to eyes, respiratory system, and skin [17]. Besides, PVdF is very sensitive to the environmental humidity, and as many fluorinated polymer at elevated temperatures, it also shows a certain reactivity against lithium metal or lithiated graphite (Li_xC_6), producing some resistive species (as LiF and $-\text{C} = \text{CF}^-$) on the electrode surface, which may trigger the onset of thermal runaway [9, 18]. All these noxious properties extend their effect on the recycling procedure of components at the end of battery life. For all these reasons, one of the goals for future research on battery technologies is the development of greener, cheaper, and electrochemically stable electrode binders [16]. Several of these problems could be solved or reduced by using water-soluble binders [15, 19–22, 38]. Typically, aqueous binders have some advantages, for example, their cost is generally low, they are eco-friendly, and can be easily disposed at battery end of life. Finally, they do not require strict control of the processing humidity, and drying speed is fast during electrode fabrication [7, 16].

Graphite-based anode electrodes are being already produced using a mixture of sodium carboxymethyl cellulose (Na-CMC) and styrene-butadiene rubber (SBR) [23–25]. Na-CMC is widely used in food industry, it is a linear polymeric derivate of cellulose and consist of β -linked glucopyranose residues with varying levels of carboxymethyl ($-\text{CH}_2\text{COO}^-$) substitution [26], where the presence of the carboxymethyl groups is responsible for the aqueous solubility of CMC [25]. The price of Na-CMC is lower than PVdF (about 1–2 euro/kg) and has the advantage to ease the recycling of LIBs electrode easier [15].

Many works report that water-soluble sodium carboxymethyl cellulose, generally combined with styrene-butadiene rubber facilitates an efficient network of chemical bonding between the conductive agent and the silicon nanoparticles. This network is able to accommodate the large volume expansion of silicon during charging, consequently improving the final capacity retention of the electrode [23, 25, 27–29].

Beyond CMC/SBR couple [15, 23–25, 30] other water-soluble binders were studied and used in LIBs: Li-CMC [22], gelatin [15, 23–25, 31–34], sodium alginate [35, 36], xanthan gum [22], chitosan and derivate [16, 37], agar-agar, carrageenan, guar gum [38], and many other polymers as PAA [39–41], PMA [42], PVA [17, 43], AMAC [44], AMMA [45], and polyimide [46]. All of them have been reported as promising new binder system for Li-ion battery replacing PVdF.

In this work, we are presenting results regarding the application of low cost, commonly used aqueous binders. The

materials, tested as anode binders, mixed with graphite to constitute the anodic slurry. They fulfill the following requirements:

- Possibility of easy scaling-up to industrial systems
- Availability
- Low cost
- No require of toxic solvents
- Easy recycling
- Electrochemical stability
- Good adhesion between particles and substrate

After a first screening based on the feasibility of the slurry prepared, we chose the following materials:

Na-alginate, derived to alginate, high-modules natural polysaccharide extracted from brown algae. Alginate contains carboxylic groups in each of the polymer's monomeric units, and this high concentration of functional (carboxylic) groups is probably a major cause of good performance as binder, especially with Si-based anodes [35].

Chitosan is one of the most plentiful natural biopolymers obtained by deacetylation of *N*-acetylglucosamine units of chitin [16, 47]. It is a biocompatible, biodegradable, and non-toxic linear polysaccharide which is soluble in water up to pH 6.2, thanks to its hydrophilic nature originated by the hydroxyl and amino groups [48].

Tragacanth gum is one of the three most important exudated gums, with arabic gum and karaya gum. It is exudated from some species of *Astragalus gummifer* shrub, widespread in some areas of Asia (Iran, Turkey, Syria). Tragacanth gum is a complex and highly branched heterogeneous polysaccharide. It consists of two main fractions: tragacanthin, which is the water-soluble fraction and bassorin or tragacanthic acid, which is insoluble but water-swallowable [49]. Tragacanth gum has been used for thousands of years in many industrial fields (texture, food, pharmaceutical) [49, 50].

Gelatin is a strong dispersion agent, widely used in food but also in pharmaceutical and photographic industries. It is an amphoteric polyelectrolyte produced by acid or alkali denaturation of collagen that contains ionizable groups such as COOH and NH_2 that make it hydrophilic and substantially insoluble in commonly used organic electrolyte solvents. When gelatin is heated up to 65 °C in water, soluble collagen and gelatin are desaturated and form random coils, generating high viscosity, which makes it suitable as an adhesion agent for bonding particles onto substrates [33, 34, 51–53].

All the listed binders were used in anodes preparation. The surface morphology was studied by means of scanning electron microscopy, and the electrochemical properties have been tested via galvanostatic cycling at different current regimes. An important characterization from the industrial application viewpoint is the rheology behavior measurement to evaluate

the suitability of these binders to the industrial processing that is to say the slurry deposition capability.

Also PVdF and Na-CMC/SBR couples have been tested in the same way to obtain a direct comparison of the performance of the studied binders with a non-aqueous (PVdF) and an aqueous binder industrially used already.

Experimental

Synthetic graphite TIMREX SLS30 (crystallinity L_c 200 nm, specific surface area $6.8 \text{ m}^2 \text{ g}^{-1}$, interlayer distance 0.3357 nm) provided by Imerys Graphite & Carbon was used as anodic active material (AM) for its good electrochemical performance and its good dispersion in water and carbon black C45 (Imerys Graphite & Carbon) as conductive additive (CA). The six water-soluble compounds used as water-soluble binders are respectively: Na-CMC/SBR couple (Daicel 2200/JSR TRD102A) in 1:2 rate, gelatin (food grade gelatin leaf, 200 bloom), sodium alginate (Aldrich-180,947), tragacanth gum (Aldrich-G1128), and chitosan (Aldrich-419,419) which were compared to the traditional PVdF with NMP solvent (Kynar 761 and Aldrich, respectively). For each binder, a 94:2:4 formulation (wt% of AM, CM, and binder) was used. The solid-water soluble binders were weighed and transferred into an appropriate beaker with 4 ml of MilliQ water, whilst for PVdF, NMP was used. The beaker was sealed, and the dispersion stirred for 4 h at 50 °C to promote solubilization. The solid fraction of graphite and conductive binder was separately mixed by a mortar and slowly added to the liquid fraction. The complete mixture was also stirred for 4 h.

Electrode preparation

The working electrodes were prepared by *solvent tape casting* method, where the slurry is mechanically deposited on the anode current collector of copper foil (Goodfellow, 0.0125 mm thickness) by means of a doctor blade adjusted for 200 μm deposition and an automatic film applicator (Sheen 1133 N) with a speed of 50 mm/s. After evaporating the solvent in air, disks of 2.54 cm^2 were punched out, vacuum dried at 150 °C (Büchi Glass Oven B-585) for 4 h, then transferred into an argon-filled dry glovebox (MBraun Labstar, H_2O and O_2 content <1 ppm) where the disks were weighed and the cells assembled. The composite electrodes were placed in a beaker-type three-electrode EL-cells with lithium foil (Chemetall Foote Corporation) as counter and reference electrode and two glass-wool disks (Whatmann GF/A) with 0.63 mm thickness each as the separator. The liquid electrolyte used is a solution 1.0 M LiPF_6 in 1:1 mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) + 1% vinyl carbonate (VC).

Electrochemical characterization

The cycling performance was investigated by means of galvanostatic discharge-charge cycling (GC) using an Arbin BT-2000 at room temperature. The potential interval ranged between 0.01 and 1.5 V vs. Li/Li^+ . Different types of cycling tests were carried out: singles cycles at low current of C/10 (theoretical capacity of graphite 372 mAh/g) to get the potential profile of the graphite electrodes at the first charge (lithiation) and following discharge (delithiation); repeated cycles at different C rate to get information on the rate performance variations with the kind of binder and continuous cycling to evaluate cycling stability.

Morphological analysis

FESEM images were taken using a Zeiss SUPRA™ 40 with Gemini column and Schottky field emission tip (tungsten at 1800 K). Acquisitions were made at acceleration voltage of 5 kV and working distance (WD) between 2.3–3.1 mm, with magnification up to 100 KX.

Rheology tests

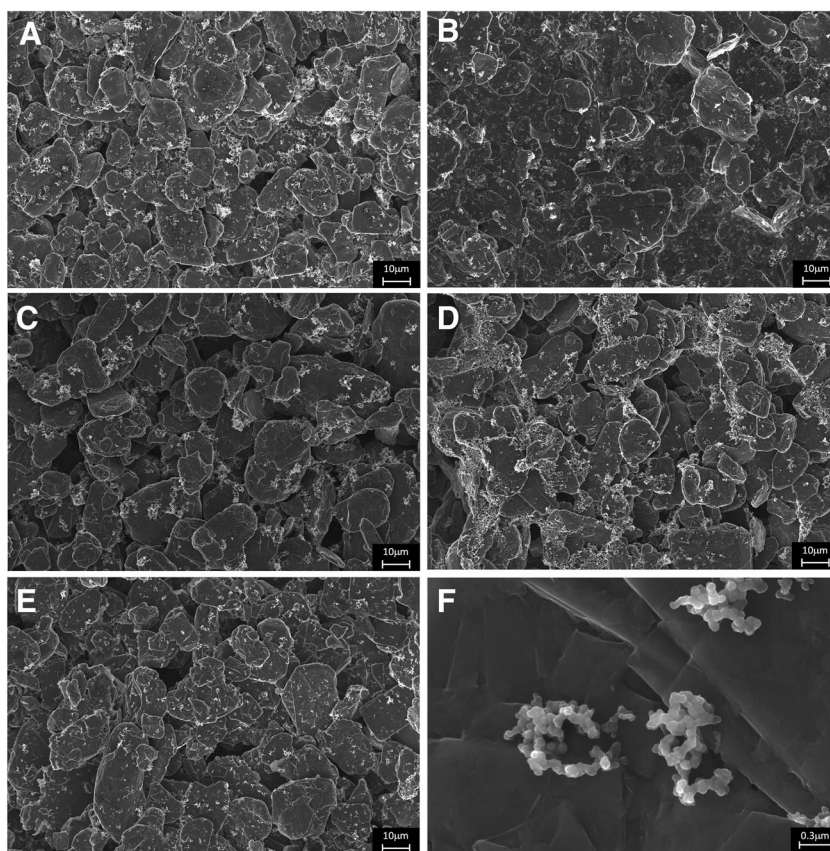
The measurements were intended to evaluate the applicability as binders of these materials to the industrial processes, and thus the rheological behavior of the electrode slurry was studied from the perspective of deposition capability. The rheological properties of the anode slurries have been measured by a Kinexus pro rheometer (Malvern Instruments Ltd) using a cone/plate geometry (60 mm of diameter and 1° angle). The measurements have been carried at the Lithops s.r.l. labs. The slurry samples have been prepared following the procedure already described.

Results and discussion

Morphological observation

FESEM images of the as prepared samples under test are reported in Fig. 1a–f. The morphological aspect is very similar in all cases: graphite particles having a size ranging between 5 and 20 μm . Carbon black nanosize particles are also well-evident, homogeneously distributed over the graphite particles. An example is reported in Fig. 1f in the case of Na-CMC + SBR sample. Such uniformity between the samples suggests a very similar electrochemical behavior. The PVdF containing electrode morphology is also very similar to the one reported in the literature [16].

Fig. 1 FESEM images of the as prepared samples: **a** Na-CMC, **b** Na-ALG, **c** chitosan **d** tragacanth, **e** gelatin at 2.5 KX magnification, and **f** gelatin at 100 KX magnification



Electrochemical results

Figure 2a reports the first charge (lithiation step) for the different graphite electrodes. As expected, the potential profile is similar for the various samples being the active material, tested in the same conditions. Differences are seen in the potential ranges 0.7–0.2 V and 0.2–0.1 V. While Na-CMC + SBR and Na-alginate show a steep decay from 1.5 to 0.1 V, PVdF and

chitosan potential profiles show processes taking place at 0.7–0.2 V and 0.2–0.1 V. Tragacanth gum and gelatin potential behave in a middle way, showing a more evident step in the interval 0.2–0.1 V only. As it is well-known, the process at higher potentials is related to the irreversible reaction of the electrolyte components at the electrode surface (SEI formation). Examination of the potential profiles of Fig. 2b indicates that this is the case for PVdF and chitosan.

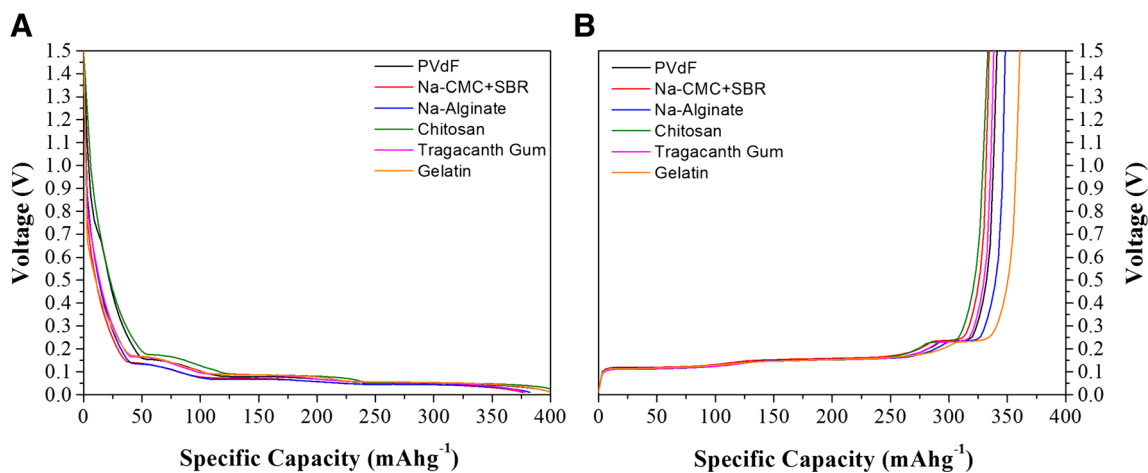


Fig. 2 Potential vs. specific capacity profiles at C/10 for the first cycle during charging (a) and discharging (b) of the six graphite electrodes with different binder

Table 1 Capacity after charge and discharge of the first cycle and coulombic efficiency for the first three cycles at C/10

Binder	Litiation capacity (mAh/g) 1° cycle	Delitiation capacity (mAh/g) 1° cycle	Coulombic efficiency (%) 1° cycle	Coulombic efficiency (%) 2° cycle	Coulombic efficiency (%) 3° cycle
Na-CMC + SBR	375	340	91	98	99
PVdF	383	342	89	97	99
Tragacanth gum	377	338	90	98	99
Chitosan	410	333	81	97	99
Gelatine	400	359	90	98	99
Alginate	380	348	92	99	99

Correspondingly, the coulombic efficiency at the first stage is the lowest for this kind of electrodes (Table 1).

At lower potentials, tragacanth gum and gelatin (but also PVdF and chitosan) show a higher pronounced step, generally corresponding to the progressive intercalation of lithium. The fact that in Fig. 2b this stage appears reduced, draws to think that at least in part the processes occurring at 0.2–0.1 V during lithiation (Fig. 2a) is irreversible. It must be noted anyway that the differences in coulombic efficiency are detectable but minimum they tend to disappear from the second cycle on showing similar high values (Table 1).

It can be interesting to note that in ref. [16], reporting results of a comparative study between PVdF and chitosan as graphite binders, chitosan appears to have a SEI formation reaction much less important than PVdF. This finding, opposite to ours, can well be justified by the different experimental conditions in which the measurements have been carried out.

The influence of the various binders on the rate performance of the graphite electrodes discharge (delithiation) is more evident than the higher is the current regime, Fig. 3.

Please insert here Fig. 3

As already seen in Table 1, the differences in performance at C/10 are hardly detectable. At C/5 the differences become more evident and also the discharging capacity order is changing: graphite-chitosan electrode improves its performance during the C/5 cycles becoming the best performing one. This characteristic is maintained at 1C discharging: gelatin, tragacanth gum, Na-alginate, PVdF, and Na-CMC + SBR follow in the order. The best results at high current are therefore shown by the biopolymers binders. In these conditions, the conductive additive (carbon black) fully exerts its action. One could therefore suggest a sort of synergistic effect between the biopolymers and the carbon additive making its action more efficient. In the case of Si, having though a different behavior from graphite, the idea of an efficient bonding network has been considered [25, 27]. The same idea could be recalled in this case also.

Other information are gathered from the duration test consisting in repeated cycling at 1C. The current regime has been chosen having in mind a future industrial application needing realistic conditions. An initial formation cycle at

lower current has been for the moment still maintained. As can be seen from Fig. 3, the various kinds of electrodes maintain, at least at the beginning, the same capacity ordering. The capacity profiles have a common trend showing a discharge capacity maximum between 10 and 20 cycles after which the capacity stabilizes at different values. The maximum being at almost the same number of cycles draws to think that it is probably a feature of the graphite used. More important is the stabilizing value at higher cycle number. Under this respect, the most performing binders are chitosan and gelatin approaching 100 mAh/g after 100 cycles. Both Na-CMC + SBR and PVdF, the comparison binders show much lower unsuitable values.

Rheology results

The viscosity of the slurries was monitored during shear rate ramp test. All rheological measurements are performed at 25 °C. A 300 s rest period is observed after the loading of the samples to have a starting point for the measurements not affected by the shear that is induced during this operation.

As shown in Fig. 4a, Na-CMC + SBR, Na-Alginate, and tragacanth gum are presenting a shear thinning behavior,

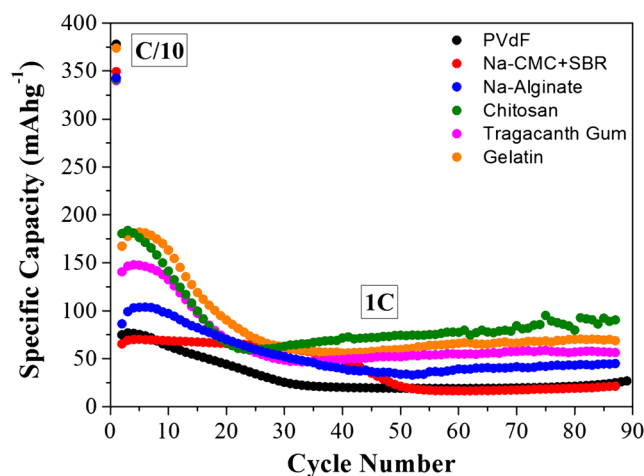
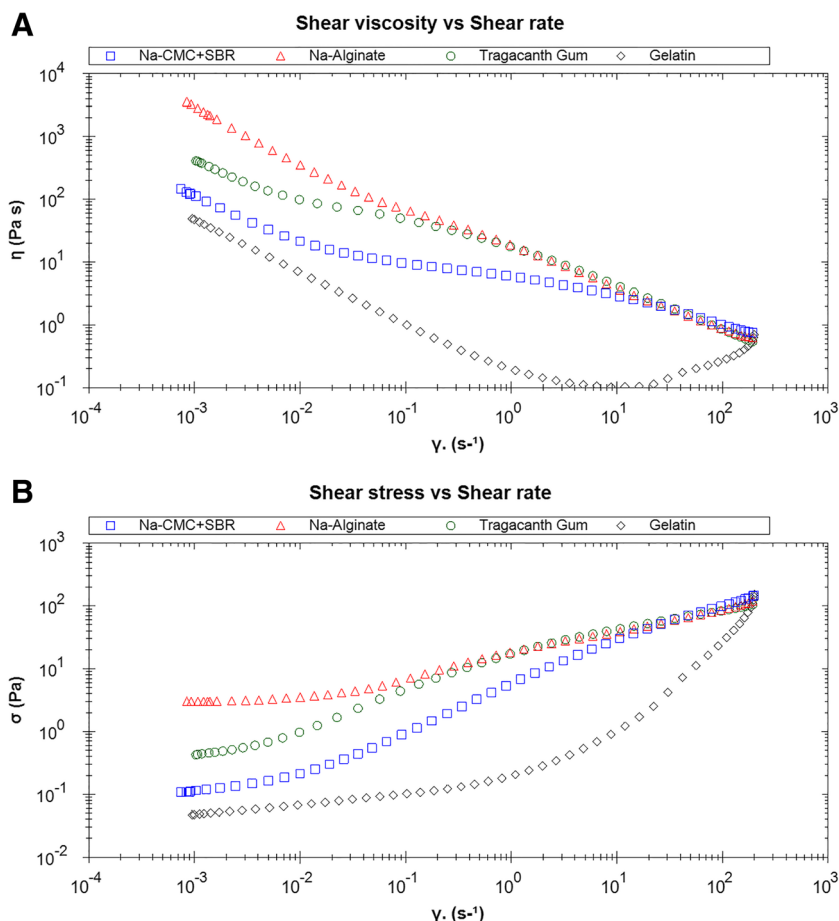


Fig. 3 Specific capacity vs. cycle number at C/10 (first cycle only) and 1C for the six graphite electrodes with different binder

Fig. 4 Evolution of the viscosity η with the increment of the shear rate γ (a) and shear stress evolution σ as function of the shear rate (b) for Na-CMC + SBR, Na-alginate, and tragacanth gum slurries



meaning that the slurry is flowing and the deposition is expected to be homogeneously distributed without defects, like stripes, on its surface. The gelatin instead is showing a shear thickening behavior that, for the chosen composition, is not suitable for the deposition of the slurry on the current collector.

The steep increase in stress for the gelatin when the shear rate is in the range of deposition can be seen in the shear stress-related graph (Fig. 4b).

Please insert here Fig. 4

It can be concluded that for the proposed formulation, as new binder for anode slurries, from the rheological point of view of the deposition on a current collector, tragacanth gum is a good candidate whereas gelatin is to be discarded.

Slurry engineering is a must in the case of gelatin binder in order to understand if it is possible to have a workable formulation suitable for industrial purposes.

Conclusions

Various biopolymer-related materials have been investigated as possible Li-ion electrode binders, in particular as graphite anode binders. Tragacanth gum has never been

taken into consideration before. Chitosan, Na-alginate, and gelatin have been already investigated, though the different experimental conditions leading to different findings. While at low regime, the galvanostatic cycling performance is not so different among the studied material and also with respect to PVdF and Na-CMC + SBR considered for comparison, at higher rate, the differences come out to the benefit of the biopolymer-related materials (chitosan, gelatin, tragacanth gum). The performance at high-cycle numbers and high current is not satisfying but the limitation seems to come from the active material itself. This issue and the possible beneficial interaction of the binder with the conductivity additive need to be more thoroughly investigate in the future. Even more important, in view of exploring the real possibility of an easy industrial upscale is the rheological testing to get information on the deposition capability. Information on the binder effect electrochemical behavior does not give a complete understanding on the performance: gelatin f.i. has proved to be one of the high performing binders but its rheological behavior in the tested conditions prevents such material to be used at industry level. In order to understand if some improvement can be made by changing the formulation of the slurry, more work needs to be done.

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References

- Bruce PG, Scrosati B, Tarascon JM (2008) *Angew Chem Int Ed* 47:2930–2946
- Li H, Wang ZX, Chen LQ, Hunag XJ (2009) *Adv Mater* 21:4593–4607
- Tarascon JM, Armand M (2001) *Nature* 414:359–367
- Goodenough JB, Park KS (2013) *J Am Chem Soc* 135:1167–1176
- Dunn B, Kamath H, Tarascon JM (2011) *Science* 334:928–935
- Yang Z, Zhang J, Kinter-Meyer MCW, Lu X, Choi D, Lemmon JP, Liu J (2011) *Chem Rev* 111:3577–3613
- Chou SL, Pan Y, Wang JZ, Liu HK, Dou SX (2014) *Phys Chem Chem Phys* 16(38):20347–20359
- Loeffler N, Kopel T, Kim GT, Passerini S (2015) *J Electrochem Soc* 162:A2692–A2698
- Maleki H, Deng P, Kerzhner-Haller I, Anani A, Howard JN (2000) *J Electrochem Soc* 147:4470–4475
- Fedorova A, Orinakova R, Orinak A, Talian I, Heile A, Wiemhofer HD, Kaniansky D, Arlinghaus HF (2010) *J Power Sources* 195:3907–3912
- Chong J, Xun SD, Zheng HH, Song XY, Liu G, Ridway P, Wang JQ, Battaglia VS (2011) *J Power Sources* 196:7707–7714
- Liu G, Zheng H, Simes AS, Minor AM, Song X, Battaglia VS (2007) *J Electrochem Soc* 154:A1129–A1134
- Choi NS, Lee YG, Park JK (2002) *J Power Sources* 112:61–66
- Li J, Daniel C, Wood D (2011) *J Power Sources* 196:2452–2460
- Lux SF, Schappacher F, Balducci A, Passerini S, Winter M (2010) *J Electrochem Soc* 157:A320–A325
- Chai L, Qu Q, Zhang L, Shen M, Zhang L, Zheng H (2013) *Electrochim Acta* 105:378–383
- Prosini PP, Carewska M, Cento C, Masci A (2014) *Electrochim Acta* 150:129–135
- Du Pasquier A, Disma F, Bowmer T, Gozdz AS, Amatucci G, Tarascon JM (1988) *J Electrochem Soc* 145:472–477
- Lee JH, Kim HH, Zang DS, Choi YM, Kim H, Yi DK, Sigmund WM, Paik U (2010) *J Phys Chem C* 114:4466–4472
- Zheng X, Li J, Singh N (2014) *Crit Rev Environ Sci Technol* 44:1129–1165
- Nie H, Xu L, Song J, Song X, Shi X, Wang X, Zhang L, Yuan Z (2015) *Green Chem* 17:1276–1280
- Courtel FM, Niketic S, Duguay D, Abu-Lebdeh Y, Davidson IJ (2011) *J Power Sources* 196:2128–2134
- Hochgatterer NS, Schweiger MR, Koller S, Raimann PR, Wohrle T, Wurm C, Winter M (2008) *Electrochem Solid State Lett* 11(5):A76–A80
- Drofenik J, Gaberscek M, Dominko R, Poulsen FW, Mogensen M, Pejovnik S, Jamnik J (2003) *Electrochim Acta* 48(7):883–889
- Buqa H, Holzapfel M, Krumeich F, Veit C, Novak P (2006) *J Power Sources* 161:617–622
- Clasen C, Kulicke WM (2001) *Prog Polym Sci* 26:1839–1919
- Lestriez B, Bahri S, Sandu I, Roué L, Guyomard D (2007) *Electrochem Commun* 9(12):2801–2806
- Beattie SD, Larcher D, Morcrette M, Simon B, Tarascon JM (2008) *J Electrochem Soc* 155(2):A158–A163
- Liu WR, Yang MH, Wu HC, Chiao SM, Wu NL (2005) *Electrochem Solid State Lett* 8(2):A100–A103
- Lee HJ, Paik U, Hackley VA, Choi YM (2005) *J Electrochem Soc* 152:A1763–A1769
- Dominko R, Gaberscek M, Bele M, Drofenik J, Skou EM, Wursig A, Novak P, Jamnik J (2004) *J Electrochem Soc* 151(7):A1058–A1062
- Drofenik J, Gaberscek M, Dominko R, Bele M, Pejovnik S (2001) *J Power Sources* 94:97–101
- Bele M, Gaberscek M, Dominko R, Drofenik J, Zupan K, Komac P, Kocevar K, Musevic I, Pejovnik S (2002) *Carbon* 40:1117–1122
- Sun J, Huang Y, Wang W, Yu Z, Wang A, Yuan K (2008) *Electrochimica Acta* 53:7084–7088
- Kovalenko I, Zdyrko B, Magasinski A, Hertzberg B, Milicev Z, Burtovyy R, Luzinov I, Yushin G (2011) *Science* 334:75–79
- Li JX, Zhao Y, Wang N, Ding YH, Guan LH (2012) *J Mat Chem* 22:13002–13004
- Yue L, Zhang L, Zhong H (2014) *J Power Sources* 247:327–331
- Cuesta N, Ramos A, Camean I, Antuna C, Garcia AB (2015) *Electrochim Acta* 155:140–147
- Magasinski A, Zdyrko B, Kovalenko I, Hertzberg B, Burtovyy R, Huebner CF, Fuller TF, Luzinov I, Yushin G (2010) *ACS Appl Mater Interfaces* 11:3004–3010
- Komaba S, Shimomura K, Yabuuchi N, Ozeki T, Yui H, Konno K (2011) *J Phys Chem C* 115:13487–13495
- Zhang ZA, Zeng T, Qu CM, Lu H, Jia M, Lai YQ, Li J (2012) *Electrochimica Acta* 80(8):440–444
- Komaba S, Yabuuchi N, Ozeki T, Okushi K, Yui H, Konno K, Katayama Y, Miura T (2010) *J Power Sources* 195:6069–6074
- Park HK, Kong BS, Oh ES (2011) *J Power Sources* 13:1051–1053
- Zhang SS, Xu K, Jow TR (2004) *J Power Sources* 138:226–231
- Zhang SS, Jow TR (2002) *J Power Sources* 109(2):422–426
- Ohta N, Sogabe T, Kuroda K (2001) *Carbon* 39(9):1434–1436
- Wang SF, Shen L, Zhang WD, Tong YJ (2005) *Biomacromolecules* 6:3067–3072
- Majeti NV, Kumar R (2000) *React Funct Polym* 46:1–27
- Fattahi A, Petrini P, Munarin F, Shokoohinia Y, Golozar MA, Varshosaz J, Tanzi MC (2013) *J Appl Polym Sci* 129:2092–2102
- Verbeke D, Dierckx S, Dewettinck K (2003) *Appl Microbiol Biotechnol* 63:10–21
- Bele M, Pejovnik S, Besenhard JO, Ribitsch V (1998) *Colloids Surf A Physicochem Eng Asp* 143:17–26
- Bele M, Pejovnik S (1999) *J Mater Sci Lett* 18:1841–1849
- Bele M, Kocevar K, Musevic I, Besenhard JO, Pejovnik S (2000) *Colloids Surf A Physicochem Eng Asp* 168:231–239