Functional binders as graphite exfoliation suppressants in aggressive electrolytes for lithium-ion batteries

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ABSTRACT

A comparative study of various electrode binders for graphite electrodes was conducted in a carbonate-based electrolyte with a high content of propylene carbonate (PC) as a means to evaluate anode degradation in presence of different binders. Because of its direct contact with the active material, a binder can be interpreted as an interfacial layer and as a local part of the electrolyte, the properties of which greatly depend on the interaction with the liquid electrolyte. In this work we demonstrate how a carefully chosen binder can create a specific surface environment that can protect graphite from exfoliation when the binder exhibits poor solubility in the electrolyte solvent and good surface adhesion to the active material. The exceptional stability of graphite electrodes containing poly(acrylic acid) sodium salt (PAA-Na) and carboxymethyl cellulose sodium salt (CMC-Na), respectively, in a PC-rich electrolyte is explained through the understanding of binder swelling and functionality. Interfacial resistances and electrochemical stability were investigated with impedance spectroscopy and galvanostatic cycling. Electrode morphologies and distributions of material were analysed with SEM and EDX. Evidence is presented that the surface selectivity increases with concentration of functional groups and polymer flexibility. Therefore only the less selective, stiff polymer with less functional groups, CMC-Na, provides sufficient protection at low binder contents.

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1. Introduction

Graphite electrodes are the most thoroughly investigated and current state-of-the-art negative electrode in lithium-ion batteries (LIB) for many electronics applications. A key feature for long cycle life and cycle stability is the formation of a stable solid-electrolyte interface (SEI) layer [1–4]. The SEI formed on a graphite electrode in carbonate-based solvents is likely the most deeply studied and best understood electrode interface [5]. The presence of relatively high contents of ethylene carbonate (EC), typically ≥ 30 vol.%, is of particular importance for reversible lithium intercalation [6–9]. However, because of the high melting point of EC (m.p. = $36\,^{\circ}$C) the possible operating temperature of the cell with these electrolytes is relatively high unless additional co-solvents or additives are used [10,11]. Its congener propylene carbonate (PC) would be more favorable by virtue of its low melting point (m.p. = $-49\,^{\circ}$C), but is associated with severe exfoliation as a result of cointercalation and decomposition into gaseous products [7].

The SEI stability can be further improved by additives [12] containing alkenyl, alkynyl or other electron withdrawing functionalities, e.g. carbonate derivatives such as vinylene carbonate (VC) [13,14] or sulfur oxides such as propargyl methanesulfonate (PMS) [15,16], due to their sacrificial role during the SEI formation.

An "artificial SEI layer" formed prior to any contact with the electrolyte or cell cycling has potential advantages e.g. regarding loss of lithium inventory, given that the approach yields a uniform, preferably thin, dense layer on the electrode. Such approaches may include the modification of graphite particles by polymer coatings [17–19] or monolayers of organic molecules [20,21].

An alternative yet conceivable method of introducing a premade protective layer is through the choice of functional polymers as electrode binders. Typically, binders are an essential component of composite electrodes, blended with active material and other additives by mechanical stirring, thus forming a thin polymer layer onto the active material. Functional polymers are expected to alter the surface chemistry of the electrode and can therefore be viewed as local electrolyte components at the electrode-electrolyte interface, which is dominated by the interaction between the polymers and its environment.

Recent efforts on Li-alloy negative electrodes, in particular silicon [22–25], have helped to understand the nature of binder

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materials and their impacts on battery performance. Because of the large volume expansion in these systems a functional binder to maintain the integrity of the electrode is of particular importance. More recently the importance of binders as valuable, but sometimes disadvantageous, electrode components has been explored in alternative lithium battery chemistries as well [26–28]. Many of these binders are seamlessly applied and provide performance improvements and enhanced stability in graphite electrodes, even though volume expansion is a relatively minor issue and grafting of functional groups to the surface of the active material is absent.

Carboxymethylcellulose sodium salt (CMC-Na) was introduced by Drofenik et al. [29] as a promising cellulose-based binder, only small quantities of which are required relative to the common alternatives. Electrodes containing this binder have been shown to provide superior performance and favorable impacts on SEI formation relative to PVdF [30]. Since then, CMC-Na has been successfully applied to various positive and negative electrode materials in lithium-ion batteries [19,30–32], as well as sodium-ion batteries [33]. An alternative binder material, poly(acrylic acid) (PAA) and its sodium salt (PAA-Na), have been widely investigated for similar properties [34–38]. Chong et al. reported significantly improved cycle life of graphite/LiFePO$_4$ cells containing either poly (acrylic acid) alkali salts (PAA-X, X=Li, Na, K) or PVdF binders [39].

In this study we compare three commonly used, water processible binders, namely CMC-Na, PAA-Na and styrene-butadiene rubber (SBR) with the common PVdF derivative, poly (vinylidene fluoride-hexafluoropropylene) (PVdF-HFP), in the same experimental set-up. In contrast to many previously referenced studies we have studied the impact of the binder on the electrode degradation and cycling stability in an 'aggressive' environment, i.e. an electrolyte with a relatively weak ability for forming a stable interface, but with better transport properties than its less aggressive counterparts. The influence of specific polymer properties was investigated and offers further insights regarding the origin of the stability improvements, particularly the binder swelling in the electrolyte solvent.

2. Experimental

2.1. Materials

Porous polyethylene (Solupor, Lydall Performance Materials) and glass fibre (Whatman GF-A) separators were dried over night at 80 °C and 120 °C, respectively, under vacuum. All other materials were used as received.

2.2. Electrode preparation and cell assembly

Electrode slurries were prepared according to a formulation of 85 wt.% coarse graphite powder (Leclanché, average particle size >10 μm), 3 wt.% fine graphite powder (KS6, Timcal, particle size <7 μm), 2 wt.% conductive additive (Super P, Timcal) and 10 wt.% binder. Poly(vinylidene difluoride-hexafluoropropylene) (PVdF-HFP, Kynar FLEX 2801, Arkema) was dissolved beforehand in N-methylpyrrolidone (NMP, Aldrich) to yield a 5 wt.% solution. A 35 wt.% solution of poly(acrylic acid) (PAA, M_w = 450,000, Aldrich, 35 wt.% aqeous solution) was deprotonated with a 4 M aqueous NaOH solution to give a 15 wt.% PAA-Na binder solution. Carboxymethyl cellulose (CMC-Na, Leclanché) and styrene-buta-diene rubber (SBR, PSBR100, Targray) were used as received. For electrodes containing altered amounts of binder, the ratio between the carbon materials remained constant. The solids were dispersed in either NMP (PVdF-HFP) or H$_2$O (CMC-Na, PAA(-Na), SBR). The quantity of liquid varied depending on the viscosity of the slurry. The slurry was mixed by planetary ball milling for 2 h and the bar

casted on copper foil (Goodfellow, 22 μm thick). After drying at 60 °C (NMP) or ambient conditions (H$_2$O) the electrodes were punched into 20 mm discs and transferred to an Ar-filled glovebox, where they were further dried under vacuum at 80 °C for 12 h.

All electrodes were tested in half cells against lithium metal in a pouch cell format with copper current collectors. The Celgard separator had an approx. size of 25 × 25 mm and was soaked with the electrolyte, which was 1 M LiPF$_6$ in either 1:1 ethylene carbonate:diethyl carbonate (EC:DEC, LP40, Novolyte) or a propylene carbonate (PC, Novolyte)-rich variety, 1:1:4 EC:DEC: PC. The latter was prepared by addition of a solution of 1 M LiPF$_6$ in PC (Novolyte) to LP40 electrolyte. A piece of lithium foil (125 μm thick, Cyprus Foote Mineral) of about the size of the separator was used as counter electrode. Three-electrode cells were also prepared containing an additional lithium metal reference electrode. The reference electrode was placed between two glass fiber separators. Electrochemical testing was started within 10 min of assembly.

2.3. Electrode Characterization

The electrodes were analysed with a Zeiss 1550 field emission secondary electron microscope (FE-SEM) equipped with an AZtec X-ray energy-dispersive silicon drift detector. SEM images and corresponding EDX maps of the samples were recorded at an accelerating voltage of 5 kV in order to minimize charging effects and degradation of binder exposed to the beam. Cycled electrodes (completely discharged) were thoroughly washed with dimethyl carbonate (DMC) in an argon-filled glove box and stored in a sealed glass vial. The exposure to air and moisture before introducing the samples into the analysis chamber was less than 2 min.

2.4. Electrochemical measurements

Galvanostatic cycling was performed on a Arbin BT-2043 battery cycler at a rate of C/10 (C = 372 mAh g^{-1}). The cells were clamped between two plates so as to maintain a constant stack pressure during the measurements and cycled between voltage limits of 5 mV and 1.5 V with the charge also limited to a maximum of 350 mAh g^{-1}.

AC Impedance spectroscopy (IS) in combination with galvano-static cycling was carried out on a versatile multichannel potentiostat (VMP-2, Bio-Logic) using graphite vs. lithium metal half-cells. Cells were cycled as previously described for 10 cycles. Impedance spectra were acquired over the range 200 kHz to 10 mHz with a peak-to-peak amplitude of 10 mV every two hours during the 11th cycle (both charge and discharge). The cells were allowed to relax at OCV for 20 minutes prior to starting the impedance measurement. Prior to cell cycling a spectrum was recorded at open circuit potential.

2.5. Swelling test

The swelling of the binders under investigation was examined by a method previously applied by Wang et al. [40] with slight modifications. Polymer films were casted in a PTFE mold from aqueous (CMC-Na, PAA-Na, SBR) or NMP solution (PVdF-HFP), allowed to dry under ambient conditions, transferred to the glove box and then dried under vacuum at 80 °C for 6 h. The polymers were immersed into an electrolyte solution consisting of 1 M LiPF$_6$ in EC:DEC (v/v = 1:1) and stored in a vial for several days in the electrolyte. The samples were then placed on a tissue in order to remove excess liquid from the polymer films and weighed in a closed container in order to stabilize the vapor pressure. The mass ratio between the sample before and after electrolyte exposure allows an approximation of the degree of swelling.