Electrochimica Acta 138 (2014) 288–293

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Using Polyisobutylene as a Non-Fluorinated Binder for Coated Lithium Powder (CLiP) Electrodes

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ARTICLE INFO

Article history:
Received 9 May 2014
Accepted 23 June 2014
Available online 30 June 2014

Keywords:
Lithium-metal battery
Coated lithium powder
Polyisobutylene
Safety

ABSTRACT

Binder formulations based on N-methylpyrrolidone/polyvinylidene fluoride (NMP/PVdF) or water/carboxymethyl cellulose (H_2O/CMC) are state of the art in the fabrication of anodes for lithium-ion battery (LIB) applications. However, in combination with metallic lithium these materials tend to degrade. Therefore, for the production and operation of anodes employing metallic lithium particles another binder system, which is flexible, chemically and electrochemically inert, inexpensive, commercially available and, especially for industrial applications, usable within a broad temperature range, is needed. Polyisobutylene (PIB) is able to fulfil these criteria. The advantages of this binder are its inert structure and its solubility in alkanes (e.g. heptane), which are inert against lithium metal, as well. In this work we will introduce heptane/PIB as a binder formulation for the preparation of electrodes from coated lithium powder (CLiP) particles. We demonstrate that CLiP electrodes fabricated with this binder system exhibit better electrochemical performance than electrodes made with NMP/PVdF or tetrahydrofuran (THF)/PVdF formulations. Furthermore, CLiP immersed in heptane/PIB show also better thermal stability compared to CLiP immersed in NMP/PVdF and THF/PVdF.

1. Introduction

Lithium-metal batteries have the potential to provide much higher specific energy compared to lithium-ion batteries. However, in the cell recharging process lithium metal tends to form dendrites, which poses a safety risk to the cell [1–5]. In a previous contribution, we have shown that coated lithium powder (CLiP) particles, pressed on a copper current collector, show significant reduced dendrite formation compared to plain lithium foil during cycling [6]. This can be explained with the higher surface area and therefore, lower local current density during lithium plating [7]. An alternative method to prepare lithium particle composite electrodes is with the help of a binder [8]. Various binders for lithium-ion battery anode materials such as graphite or silicon are known [9–12]. Polyvinylidene difluoride (PVdF), soluble for example in N-methyl-2-pyrrolidone (NMP), is a common binder for these electrode materials [13].

A problem, however, is the possible reduction of PVdF by lithiated graphite or metallic lithium, under the formation of LiF and C=CF- double bonds, at elevated temperatures [14,15] leading to an exothermic reaction [16]. Furthermore, PVdF can show tendencies of swelling or dissolving when exposed to organic solvents, which are also used in LIB electrolytes [17–19].

Various water based binders are under investigation to replace the widely used NMP/PVdF formulation in the electrode preparation process. Investigated binders are, amongst others, polyacrylic acid (PAA) [20], polyethyleneimine (PEI) [21], poly(ethylene-co-acrylic acid). (PEAA) as well as styrene butadiene rubber (SBR), poly(vinyl pyrrolidone) (PVP) or carboxylmethyl cellulose (CMC) [22–26]. Poly(acrylamide-co-diallyldimethyl-ammonium-chloride) (AMAC), [27] polytetrafluoroethylene (PTFE) [28] and poly(acrylonitrile-methyl methacrylate) (AMMA) [29,30] have also been tested. The water based binders, which combine well with LIB anode materials, are not suitable for the fabrication of anodes containing metallic lithium, because lithium would react violently in a water-based slurry. As mentioned before NMP/PVdF formulations have the disadvantage to react with metallic lithium. NMP as processing solvent for PVdF can be replaced by alternative solvents, which are less reactive against lithium, such as tetrahydrofurane

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http://dx.doi.org/10.1016/j.electacta.2014.06.128
0013-4686/

(THF). THF dissolves reasonable amounts of PVdF at an elevated temperature of 80 °C [31] Another binder, which is also used in LIBs, is polyisobutylene (PIB) [32–34]. PIB is chemically and electrochemically inert and non toxic. It is flexible and can be used in a broad temperature range. Additionally the processing solvent (e.g. heptane) is inert against lithium metal and thus can be used in manufacturing processes involving metallic lithium species such as CLiP. These properties make the formulation heptane/PIB a highly promising candidate for CLiP electrode preparation. In this contribution we report on the application of heptane/PIB in the preparation of CLiP anodes and compare the performance with NMP/PVdF- and THF/PVdF- based formulations.

2. Experimental

2.1. Materials

Coated lithium powder (CLiP, particles with an average diameter of 50 μm) and lithium foil were supplied by Rockwood Lithium. PIB (Oppanol B200) was obtained from BASF, PVdF (Kynar 761A) was received from Kynar. The solvents THF, heptane and NMP (extra dry over molecular sieve) were purchased from Acros Organics. All materials were used as received, if not stated otherwise. Binder formulation and electrodes were prepared in a dry room (0.02% moisture content).

2.2. Preparation of microstructured electrodes using different binder systems

Solutions of PIB (5 wt.%) in heptane and PVdF (5 wt.%) in NMP were prepared by stirring at room temperature overnight. CLiP (95 wt.%) was added and mixed, with a Vortex setup for 1 min., until a homogenous suspension of the binder formulations and CLiP was obtained. No reactions were observed during this time. The slurries were casted with a thickness of 200 μm on a dendritic copper foil (Schlenk, 18 μm thickness) current collector. The THF/PVdF (5 wt.%) mixture was heated to 80 °C for 3 h in a pressure-proved Schlenk tube. After cooling down to room temperature CLiP (95 wt.%) was added and mixed with a Vortex until a homogenous suspension was achieved (1 min.). Subsequently, the obtained suspension was casted onto copper foil. After drying at 70 °C in vacuum for 48 h, electrodes of 12 mm diameter were punched out. All prepared CLiP electrodes had mass loadings of around 3 mg.

3. Methods

The electrochemical measurements were performed using adapted Swagelok® cells with a three-electrode setup.

3.1. Cyclic voltammetry (CV) with CLiP as counter electrode

The produced CLiP electrodes were used as counter electrode (CE). A graphite electrode (90 wt.% Timrex SLP30, Timcal, 5 wt.% PVdF Kynar 761A, Kynar, 5 wt.% Super C65Li, Timcal) casted on copper foil (Schlenk, 18 μm thickness) with an active mass loading of around 2.5 mg was used as working electrode (WE). As reference electrode (RE), lithium foil (Rockwood Lithium) was used. Ethylene carbonate (EC)/diethylcarbonate (DEC) in a weight ratio of 3:7 with 1 M lithium hexafluorophosphate ($LiPF_6$) as conductive salt (LP47, UBE, battery grade) was used as electrolyte. Cyclic voltammetry measurements were performed at 20 °C using a VMP3 (Bio-Logic) potentiostat. The cells were cycled with a scan rate of 25 μV/s, in a potential range between 0.01-1.6 V vs. Li/Li^+.

3.2. Stripping/plating of lithium

Stripping/plating measurements were performed at 20 °C using a MACCOR battery cycler (MACCOR Series 4000). Non-dendritic copper foil (Schlenk, 10 μm thickness) was used as CE and CLiP as WE. Lithium foil was used as RE and LP47 as electrolyte. A current of 0.2 mA or 0.4 mA was applied to the electrodes for 100 cycles. Each cycle consisted of a stripping and a plating step with a duration of one hour.

3.3. Scanning electron microscopy (SEM)

A CARL ZEISS AURIGA MODULAR CROSSBEAM workstation was used to carry out the SEM analyses. The electron source was a SCHOTTKY field emission gun with a GEMINI column. Images were taken at 3 kV accelerating voltage using an in lens detector. The lens aperture was 30 μm and the working distance 2 mm. For the SEM images Swagelok cells were disassembled in an argon filled glovebox and the CLiP electrodes were washed with diethylcarbonate (DEC) (UBE, battery grade) to remove the high viscosity EC and the conducting $LiPF_6$ salt from the surface of the electrode. DEC was removed by evaporation in vacuum. The electrode samples were transferred from the glove box to the SEM under protective argon atmosphere in a self-built transportation device. In this way, the exposure to oxygen and moisture was avoided.

3.4. Differential scanning calorimetry (DSC)

DSC measurements were carried out using a Radex instrument (Systag). Samples of about 2 g were weight into stainless steel autoclaves in an Ar-filled glove box. The samples were heated with a rate of 45 K/h from 50 °C to final temperatures of 200 or 250 °C.

3.5. X-ray photoelectron spectroscopy (XPS)

The XPS measurements were performed on an Axis ultra DLD (Kratos) using monochromatic Al Kα radiation (1486.7 eV). An area on the sample surface of about 300 μm x 700 μm was irradiated at three different points. The core scans were performed at a pass energy of 20 eV using electrostatic mode.

CLiP (50 mg) was immersed in NMP (1 ml), heptane (1 ml) and THF (1 ml), respectively. The suspensions were mixed with a vortex for 2 min. Afterwards the solvent was removed in vacuum. The dry CLiP samples were attached to the XPS sample holder with double-sided conductive carbon tape and were transferred from the dry room in sealed containers into the vacuum chamber of the XPS. The instrument as well as the transfer box is operated under argon atmosphere (ArW5, Argon with 5% hydrogen). In the following data analysis the spectra were calibrated against the Li 1s signal at 55 eV. This has been preferred because the carbon species were not unequivocally determined and the Li species was assumed to be basically organic occurring at the same energy range in all samples.

4. Results and Discussion

Electrodes containing CLiP with different binder formulations NMP/PVdF, THF/PVdF and heptane/PIB were casted on a copper current collector. During this processing step, the NMP/PVdF and CLiP slurry turned black when the casting was not performed fast enough, likely caused by a reaction between CLiP and the binder formulation. Using the combination THF/PVdF apparently solved this problem (no coloration), but led to other challenges. THF dissolved PVdF in suitable amounts only after stirring for 3 h at 80 °C. When cooling down the solution to room temperature PVdF can crystallize and precipitated again. Another challenge of this system was