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Improvement in hydrophobicity of olivine lithium manganese iron phosphate cathodes by SiF_4 treatment for lithium-ion batteries

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ABSTRACT

In this report, we successfully demonstrate a novel SiF_4 treatment on lithium manganese iron phosphate cathode (LMFP) that can significantly improve its hydrophobic property. The effect of SiF_4 treatment on the structure and hydrophobicity of LMFP powder was studied by X-ray diffraction, Fourier transform infra-red spectroscopy, scanning transmission electron microscopy–energy dispersive X-ray spectroscopy, Karl Fisher titration, and thermo-microbalance gravimetric studies. The SiF_4 treated LMFP cathode shows a substantial decrease in moisture adsorption by up to half of the untreated LMFP under ambient conditions. The SiF_4-treated LMFP also shows excellent cycle life when cycled in lithium-ion full cells, even after exposing the electrodes to ambient conditions for one day, while the untreated LMFP showed a decrease in cycle life after the same exposure.

1. Introduction

Lithium-ion batteries have revolutionized the portable consumer electronics market and are currently the preferred energy storage technology for use in hybrid, plug-in, and pure electric vehicles [1,2]. Most of the commercial Li-ion batteries for consumer electronics application use $LiCoO_2$ cathode, graphite anode, polyethylene–polypropylene separator, and $LiPF_6$ salt dissolved in carbonate solvents as electrolyte. $LiCoO_2$ cathode is commonly used cathode because of its high operating voltage (~4.0 V), high volumetric energy density due to high crystal density (5.1 g/cm^3), ease of synthesis, and good cycle life [3,4]. On the other hand its high cost, poor thermal stability and toxicity prevent its application in large scale batteries [5,6]. A step change in energy density, cost, life time, and safety of lithium-ion battery is required to make electric vehicles economically attractive when compared to conventional internal combustion engine driven vehicles. Currently layered oxides such as $LiNi_xMn_yCo_{1-x-y}O_2$ (NMC), $LiNi_{0.80}Co_{0.15}Al_{0.05}O_2$ (NCA), spinel $LiMn_2O_4$ (LMO), and olivine $LiFePO_4$ (LFP), are used in electric cars [7,8]. However, layered metal oxide cathodes suffer from poor thermal stability, as the cathode undergoes a structural change in its charged state accompanied by evolution of oxygen which can react exothermally with the electrolyte solvents resulting in catastrophic cell failure [9–11]. In this aspect, LFP cathodes with its strong covalent PO_4 bonds offer good structural and thermal stability with no oxygen release during thermal abuse, in addition to low cost (no rare earth metal raw materials), and good cycle life [12,13]. However, the energy density of LFP cathode is lower when compared to NMC cathodes, which can be increased by substituting part or all of the Fe with Mn forming $LiMn_yFe_{1-y}PO_4$ (LMFP) cathodes, as the operating voltage of $Mn^{2+/3+}$ redox couple is 4.1 V vs. Li/Li$^+$ when compared to 3.4 V for $Fe^{2+/3+}$ [14–16].

Since lithium metal phosphate cathodes have intrinsically lower electronic and ionic conductivity, various strategies such as syntheses of nanoparticles, doping, and coating with conductive carbon have been pursued to ameliorate it [17,18]. The nano-sized particles and porous carbon coating, however, result in olivine cathodes with two orders of magnitude higher surface area than conventional NMC cathodes (up to 35 m^2/g for olivine phosphates compared to ~0.50 m^2/g for NMC). In spite of its low surface area, even NMC and NCA cathodes are known to be somewhat reactive with CO_2 and H_2O under ambient conditions forming Li_2CO_3/LiOH on the cathode's surface, which in turn attracts more H_2O due to its hydrophilic nature [19,20]. Therefore, high surface area in olivine phosphate could cause rapid adsorption of water when exposed to ambient humidity. This in turn will lead to poor lithium-ion cell performance, as any trace amount of water in the cathode will react with $LiPF_6$ salts in the electrolyte resulting in the formation of HF acid that leads to metal dissolution, electrolyte decomposition, and gas generation in the cells [21,22].

Consequently, the effects of ambient condition exposure on the structure, surface composition, and electrochemical performance of $LiFePO_4$ cathodes have been studied extensively in recent years [23–26]. It has been shown that on exposure to air, $LiFePO_4$ powder

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reacts with O_2 and H_2O resulting in de-lithiation and the formation of Fe^{3+} compounds and $Li_xFePO_4(OH)_x$ impurity phases on the surface leading to reduced capacity and shortened cell life and much rapid aging was observed at higher temperatures. Because of the detrimental effects of moisture adsorption on olivine phosphate cathodes, recommendations are made to always store $LiFePO_4$ powders in a dry atmosphere. Most of the battery manufacturers, therefore, employ dry rooms for cell fabrication and electrolyte filling, but powder handling, electrode slurry preparation, coating, and calendaring are generally carried out under ambient conditions where there is a significant chance for moisture adsorption. Therefore, there is a great need to develop olivine phosphate cathodes with high tolerance to moisture.

To the author's knowledge, there has been no solution presented in the literature so far to overcome the moisture adsorption problem of olivine cathodes. To generate hydrophobic inorganic materials, typically siloxanes based polymer coatings have been employed due to their ability to provide very low surface energy non-polar surfaces [27,28]. Most of the hydrophobic siloxane coatings are carried out, in literature, using siloxane/silane precursors in solvents such as alcohols or DI water, but exposing calcined olivine phosphate cathodes to solvents, especially water at high temperature could lead to oxidation/loss of lithium ions from the cathode surface [23–26]. Therefore, in this article, we have employed a completely solvent/water free SiF_4 gas treatment for forming hydrophobic siloxane on LMFP cathodes. The SiF_4-treated LMFP showcased a significant decrease in moisture adsorption over untreated LMFP and demonstrated stable room temperature and elevated temperature cycle life performance in lithium-ion pouch cells even after exposure to humid ambient conditions.

2. Experimental

2.1. SiF_4 treatment of LMFP powders

Lithium manganese iron phosphate used in this study, compositionally close to $LiMn_{0.80}Fe_{0.20}PO_4/C$ (LMFP) was synthesized as explained elsewhere [29]. SiF_4 treatments of LMFP powder were carried out in open graphite tubes inside a sealed fused silica reactor at a constant pressure of 50 mm Hg of SiF_4 gas at 300 °C for 1 h. Each tubular graphite insert (19 mm outer diameter (OD) × 9″ length (L)) was loaded with ~10 g of LMFP powder and placed into separate 1″ OD × 16″ L fused silica tubes which were connected to the gas manifold of the reactor. The tubes were lowered in to the furnace, a vacuum was pulled in the system with mechanical pump to ≤2 mm Hg and a leak check was performed. The furnace temperature was ramped at 1 °C/min to 200 °C while maintaining vacuum with a mechanical vacuum pump. The tubes were held at 200 °C under vacuum for 1 h at which point SiF_4 was added to reach the desired pressure of 50 mm Hg. The tubes were held under constant SiF_4 pressure at 200 °C for 60 min, then ramped to 300 °C and held for an additional 60 min, before being quenched by removal from the furnace.

2.2. Characterization

X-ray diffraction (XRD) data were collected using a Bruker D8 Advance θ–θ X-ray diffractometer equipped with a copper sealed-source tube and Vantec-1 linear position sensitive detector. The tube was operated at 35 kV and 45 mA and the samples were illuminated with copper K_α radiation ($l = 1.541$ Å). XRD data were collected with a 3° detector window from 15° to 70° 2θ, with a step size of 0.0256° and 1 s/step collection time. Elemental analysis of the samples was determined by inductive coupled plasma atomic emission spectroscopy (ICP-AES, Perkin Elmer 7300). Specific surface area was determined by nitrogen adsorption as per the Brunauer–Emmett–Teller (BET) theory using a Micromeritics surface area anaylzer. Scanning transmission electron microscopy–energy dispersive X-ray spectroscopy (STEM–XEDS) analysis was performed with Bruker AXS XFlash 5030 X-ray energy dispersive detector and electron energy loss spectroscopy (EELS) analysis was performed with Gatan Enfina Energy-Loss Spectrometer. Moisture adsorption analysis of the LMFP powders was carried out by Karl Fisher titration (KF) using a Metrohm model 851 coulometric titrando system at a temperature of 190 °C for 10 min. Infrared spectroscopic analysis was performed by measuring the infrared transmission spectra of the samples prepared as KBr pellets at 4 cm^{-1} resolution. The samples were measured in duplicate using a Nicolet Nexus 870 FTIR spectrometer. pH of the cathode powder was measured by adding 2 g of LMFP cathode in to 50 ml of DI water and stirring it for 30 min, followed by pH measurement.

The Karl Fisher sample preparation was as follows: LMFP was carefully sealed under a N_2 atmosphere in a Mylar bag after being formed or treated (i.e., after calcination and/or after being subsequently SiF_4 treated). The bag was opened and about 1 g samples of LMFP were placed in 6 ml Metroohm vials which were left open to ambient conditions (~50% relative humidity) and then capped at designated time intervals of 0 min, 60 min, 5 h, and 1 day.

Continuous moisture adsorption/desorption analysis was carried out in a thermo balance under controlled humidity constructed from a Cahn 1000 electrobalance, a temperature controlled furnace and a gas manifold. Six strips of coated electrodes on carbon coated aluminum foil (weight of active material around 1.0 g) were suspended in from the balance in the controlled temperature zone of the gas manifold. The electrodes were initially dried under flowing N_2 atmosphere at 130 °C for 12 h and then the chamber was cooled to 26 °C and switched to ~40% humid air. Humidified air (~40%) was generated by bubbling air through a gas dispersion tube immersed in room temperature water, flowing it through a 12 °C condenser (forming saturated air at 12 °C) and then rewarming it room temperature before flowing it into the sample chamber controlled at 26 °C. The weight gain of the electrodes with the flow of humid air was measured for 12 h. The cycle of drying in N_2 and humid air exposure was repeated once to study moisture re-adsorption properties of the electrodes.

2.3. Electrochemical analysis

Electrochemical testing was carried out by coating the LMFP active materials on carbon coated aluminum foil. The slurry was prepared by mixing appropriate quantities of active material (93 wt.%), conductive carbon (2 wt.%) and PVDF (polyvinylidene-difluoride) binder in NMP (N-methylpyrrolidone) (5 wt.%) and spread on the foil using a doctor blade. The electrodes were dried in an oven at 80 °C under ambient for about 30 min to evaporate NMP. The electrodes were punched, roll pressed, and dried overnight at 125 °C in a vacuum oven before being assembled into half cells or full pouch cells. The cathodes were assembled in to 2032 type coin cell coupling with lithium metal for half cell (capacity — 2 mAh) and AGP-2 graphite anode at an anode/cathode ratio of 1.1 for pouch full cells (capacity — 50 mAh). The electrolyte used was 1.2 M $LiPF_6$ salt dissolved in ethylene carbonate (EC)/ethyl methyl carbonate/EMC (1:3 wt.%) with 2 wt.% vinylene carbonate (VC). A commercially available polyethylene separator was used.

3. Results and discussion

Fig. 1 shows the Karl Fisher moisture analysis of untreated and SiF_4-treated LMFP after exposing the powders to ambient atmosphere (50% relative humidity) for different time intervals. It can be seen that both the untreated and SiF_4-treated LMFP picks up water rapidly during the initial stages and within 2 h of air exposure both samples pick up about 1000 ppm of water. After 1 day of air exposure, untreated LMFP picks up about 4250 ppm of water, while SiF_4-treated LMFP picks up only 2700 ppm of water demonstrating significant decrease (37 wt.%) in moisture pickup. After 1 day, moisture pickup slows due to saturation and with further exposure for 5 days untreated and SiF_4-treated LMFP demonstrated about 5140 ppm and 3200 ppm of water pickup,