Development of a Chemically Resistant Coating for a Novel Fiber Optic Temperature Sensor embedded in Lithium-ion Batteries

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ABSTRACT

Temperature is a key parameter in the safe operation of lithium-ion batteries (LIBs). In this paper, we present a novel optical fiber temperature sensor design and fabrication process that can operate within LIBs. The optical fiber is coated with two materials, a temperature sensitive layer and a protective layer. The temperature sensitive coating is polymethylmethacrylate (PMMA), which is highly sensitive to the organic electrolyte solution within LIBs; thus requiring a second protective layer. The chemically resistant protective coating is a fluorinated polymer AL-2233, which is a Teflon-like polymer able to resist organic solvents. The presented results demonstrate the performance of the temperature sensor between 24 to 32 ºC, as well as its resistance to organic solvents.

Keywords: lithium-ion batteries, fluorinated polymer, embedded fiber optic sensors, temperature monitoring

1 INTRODUCTION

Lithium-ion batteries are ubiquitous in modern day life, with their market value set to reach more than $65 billion USD in 2023 [1]. Temperature is a key parameter in the safe operation of lithium-ion batteries (LIBs) [2]. Yet to monitor battery temperature, we are still reliant on using sensors which are often attached to the exterior of a battery casing. Developing a method which accurately but also safely measures the temperature of a lithium-ion battery is paramount as more and more devices become mobile and hence reliant on lithium-ion battery technology. This is especially important as demonstrated by the global recall of the Samsung Galaxy Note 7 which was caused by overheating batteries and estimated to have cost over $5 billion USD [3].

An intensity-based optical fiber temperature sensor has been considered as the ideal candidate for internal monitoring of temperature. Optical fibers are relatively cheap, lightweight, and reliable. To enhance the temperature sensitivity of an optical fiber, a thin coating of polymethylmethacrylate (PMMA) is applied to the selected sensing region. PMMA has a reflectivity which varies with respect to temperature [4] which is desired for this application. However, PMMA is chemically susceptible to the organic electrolyte solution found inside LIBs. To counteract this, a chemically resistant coating is required to protect the PMMA layer. This would allow for the insertion of the sensor within LIBs allowing for in-line temperature sensing.

2 MATERIALS AND METHODS

The protective coating applied to PMMA needs to fulfill three criteria. Firstly, it needs to act as a protective barrier between the organic electrolyte solution and the PMMA. Secondly, it needs to be inert and not react with PMMA when applied. Thirdly, it needs to still allow for the PMMA to display the same temperature dependent properties.

Theoretically, a SiO_2 derived coating will be ideal for the PMMA region as SiO_2 has been proven to have chemically resistant properties [5]. The concern with using a SiO_2 derived coating is that the chemicals used to fabricate it are often a mixture of organic solvents (ethanol and 2-propanol), hydrochloric acid (HCl) and tetraethyl orthosilicate (TEOS) [5]. Whilst this is not a problem for coating a substrate made of glass, the mixture of organic solvents and HCl will likely strongly react with the PMMA, thus rendering the intended use not possible.

For these reasons, a polytetrafluoroethylene[1] (PTFE) coating would be best as it is highly hydrophobic due to the electronegativity of fluorine and also highly unreactive due to the carbon-fluorine bonds present. However, applying a PTFE coating to a fiber optic cable is relatively difficult as the typical process involves not only sandblasting the application area, but also baking in an oven [6]. Thankfully, there are other simpler solutions.

AL-2233 (AL-2233-1%, Fiber Optic Center) is another fluorocarbon which is suspended in a solvent [7]. This removes the need for sandblasting the delicate PMMA and also the need to bake the finished part as the solvent readily evaporates at room temperature. Additionally, the coefficient of thermal expansion of AL-2233, $2 \times 10^{-4}\,K^{-1}$ [7], is similar to PMMA's, $2.1 \times 10^{-4} K^{-1}$ [8]. This is important as the coating should not experience a large local strain due to the expansion of the inner layer of PMMA. Therefore, the

[1] PTFE is commonly marketed under the tradename Teflon™ by Chemours.

increase in length for the two layers will not only be very similar but also on the scale of $1 \times 10^{-9}\ m\,K^{-1}$ as the two coating thicknesses will be on the order of $1 \times 10^{-5}\ m$.

2.1 Investigation of Interaction between AL-2233 and Acetone

In order to test if the AL-2233 layer will protect the fiber from the electrolyte, acetone was used. Acetone and dimethyl carbonate (a common electrolyte component) both have a Hildebrand parameter of 20.3 [9], which is a quantified value describing the interaction between a solvent and a polymer.

To test AL-2233 experimentally, two drops of AL-2233 solution were placed in 2 locations on a glass petri dish. The AL-2233 was left to dry on a hot plate set to 70 ℃ which was ramped up to 100 ℃ over the course of 10 minutes, as per the manufacturer's recommendation [7]. This yielded a thin film layer of AL-2233 which can be seen in Figure 1a.

A drop of acetone was placed on the AL-2233 thin film and the results were observed under a microscope. As acetone is relatively volatile, it immediately began boiling off the surface of the thin film. A small droplet (see Figure 1b) with a reduced rate of evaporation remained due to changes in wettability of the surface increasing adhesive forces [10].

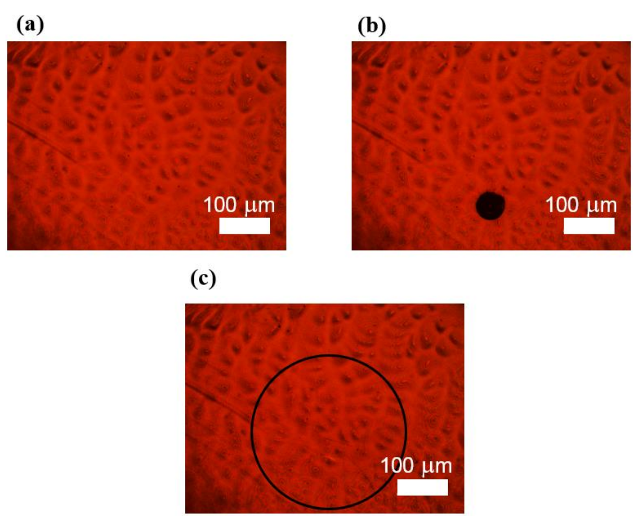

Figure 1: (a) Initial AL-2233 film (b) AL-2233 film after acetone application (c) AL-2233 film after bubble removal

In order to promote the evaporation (and potential further reaction) of the acetone, a heated air gun was used and initially set to 100 °F (37.8 ℃). When it was seen that this heat was not sufficient, a higher temperature of 150 °F (65.6 ℃) was used. Even at this elevated temperature, the micro-droplet did not evaporate. To remove the droplet completely, a paper towel was used. An image of the post-acetone AL-2233 thin film was taken (Figure 1c).

When comparing the before and after images, it was seen that the surface did not appear to have changed. The only difference between Figure 1a and c is the fine scratches caused by the paper towel's fibers (circled in black).

Figure 2a is a plastic petri dish which had a thin film of AL-2233 deposited on it using a pipette. When acetone was placed on the plastic, the reaction was clear, and the plastic became discoloured. However, when the acetone reached the AL-2233 boundary, it was unable to pass over it. This is shown by the sharp change of direction of the discoloured plastic. Figure 2b is the highlighted region of the Al-2233 boundary from Figure 2a. The damage caused by acetone on the plastic surface can be clearly seen in the top half of the image, while the area of the AL-2233 has been protected from solvent.

These two pieces of evidence prove that AL-2233 provides protection from acetone. This then infers that the AL-2233 coating should likely provide protection from other organic solvents, namely the electrolyte solution of the lithium-ion battery.

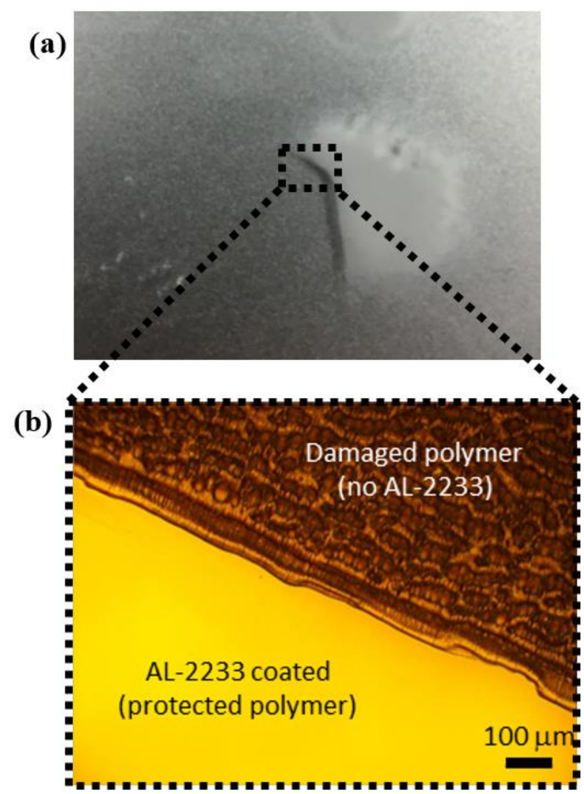

Figure 2: (a) Acetone interacting with AL-2233 boundary (b) Acetone interacting with AL-2233 boundary 10x magnification

2.2 Optical Fiber Surface Preparation and Coating Application

The sensing region of the fiber-optic sensor was chosen to be 2 cm in length. This length was chosen so that we are able to average the temperature over a 2cm region inside the LIB, giving us a more reliable reading. The protective polymer coating in this region is stripped using fiber strippers and acetone [11]. Next, the fluorine-doped silica cladding on the sensing region is removed through hydrofluoric (HF) etching. This is then followed by ozone cleaning, which eliminates any radicals present after the etching process.

The PMMA coating was then applied using a mechanical drag coating method which was found to yield a homogenous coating. The experimental setup for the mechanical drag coating method is found in Figure 3. It is worth noting that for producing the PMMA layer, a bubble containing approximately 0.5 mL solution of acetic acid and PMMA is placed on a glass slide in place of the capillary tube. The fiber is placed in line of the bubble and clamped. The motorized stages were connected to a computer running a MATLAB script, allowing the bubble to slide along the fiber, creating the PMMA layer. The overall range of the stages was approximately 25 mm (as per the manufacturer's documents). The coating process took about 2 minutes to complete.

The AL-2233 solution has a very low viscosity and forming a bubble of this solution for coating was impossible. Therefore, we decided to use a a capillary tube filled with AL-2233 solution in place of the glass slide in the same mechanical drag coating apparatus used for PMMA coating (Figure 3). The coating process took multiple attempts to determine the number of cycles and motor speeds required for a uniform coating. Additionally, in order to obtain a uniform coating around the circumference of the fiber, the fiber had to be placed in the middle of the capillary tube which was a relatively challenging task to achieve. Once other parameters such as drying time between coatings were determined, it took about 7 minutes to complete the coating process.

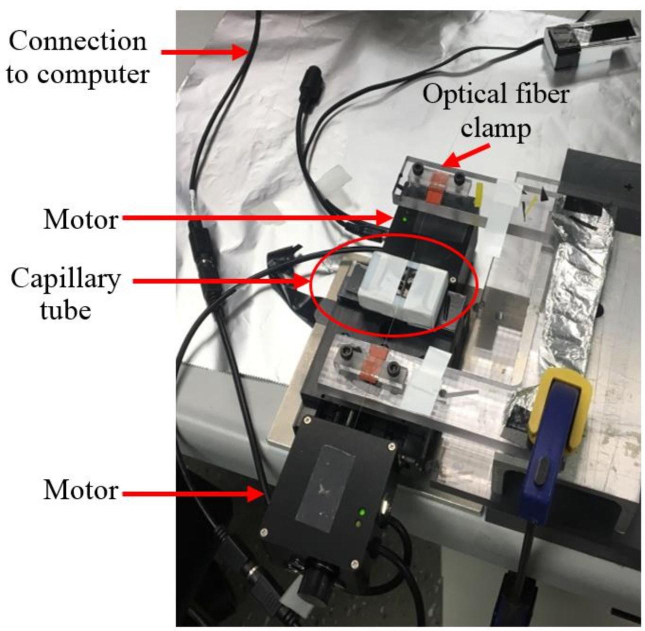

Figure 3: Coating apparatus for AL-2233

3 RESULTS AND DISCUSSION

To understand the effect of AL-2233 on the sensing mechanics, an optical fiber coated with PMMA acting as a temperature sensor was coated with AL-2233. PMMA is a polymer that demonstrates a decrease in its refractive index as temperature increases [12]. The sensing region of the fiber was placed inside a water bath, where temperature was monitored with a k-type thermocouple. This setup was then placed on top of a Peltier stage (Ferrotec 9501/128/040B) and the temperature of the stage was controlled using a PID temperature controller (Ferrotec FTC 100).

Figure 4 shows the general observed trend of the optical transmittance which increases linearly with temperature. Since both PMMA and AL-2233 have similar thermal expansion coefficients, the thermal expansion of PMMA is left unhindered. As the PMMA coating expands, the refractive index of it also changes and this change is linear over the tested temperature range [12]. Therefore, as the temperature changes, the refractive index changes causing a change in the optical signal transmission.

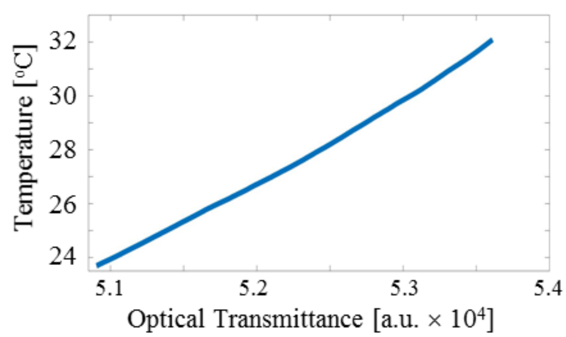

Figure 4: Optical transmission of the sensor vs. temperature reading of the thermocouple

The effect of AL-2233 on PMMA was studied extensively in order to verify that the structure of PMMA was not affected by AL-2233. Figure 5 shows that the thickness of the fiber increases after each coating application step as expected. This therefore indicates that the method used to apply the AL-2233 is appropriate as the thickness of the fiber did not decrease, meaning that the carrier solvent of the AL-2233 did not react with the PMMA layer. When the AL-2233 coating method was tested on a clean uncoated fiber, approximately 2 μm of AL-2233 was deposited, so our results are further consistent with the expected coating thickness.

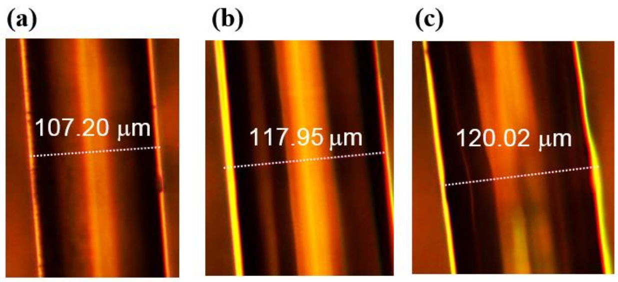

Figure 5: (a) Initial etched fiber (b) Fiber coated with PMMA (c) Fiber coated with PMMA & AL-2233

4 CONCLUSIONS

We have presented a fabrication process for a chemically resistant fiber-optic temperature sensor that can be embedded within Lithium-ion batteries. One of the greatest challenges was to obtain a uniform coating of AL-2233 that fully covered the sensing region on the optical fiber. Since the AL-2233 solution used only had a concentration of 1%, the coating process was even more complicated. However, we were able to overcome these challenges through our innovative capillary tube motor drag coating method. Using this method, the application of AL-2233 was tested onto a PMMA coated optical fiber and found to not effect the original PMMA coating. The results demonstrate that the chemically resistant layer made of AL-2233, a fluorocarbon, is resistant to acetone, which is a strong organic solvent. An optical fiber sensor coated with both PMMA and AL-2233 was tested for sensitivity to temperature and found to display the same behavior as a fiber-optic sensor coated with PMMA only, where increasing temperatures increases the intensity of the transmittance through the fiber. Future work will focus on improving the uniformity of the AL-2233 coatings to ensure its resistance to battery electrolytes before embedding them into the LIBs.

ACKNOWLEDGMENTS

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