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Surface Modification and Fabrication of Li-ion Battery Components for Plug-in Hybrid Electric Vehicle

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This paper addresses an important issue for the practical application of lithium ion batteries in PHEV. More specifically, preliminary research results on the coating of separators, welding of battery tabs, and fabrication and surface featuring of anodic and cathodic current collectors are presented. These developments aim at improving the power performance, reliability, and safety of lithium ion batteries.

Introduction

Since its revolutionary introduction into the portable electronics market by Sony in 1991, lithium ion cells have enjoyed a constantly increasing market share. This raised the expectations for its implementation in PHEV, particularly with the heightened needs for alternative energy and environment protection. However, even though the basic chemistry and design of Li-ion PHEV cells are quite similar to those of small consumer cells, the major challenge for PHEV cells is the demand for much higher power performance. Furthermore, this demand is also linked to the safety/abuse resistance, operating life (including calendar life and cycle life), and cost of manufacturing. Li-ion battery components such as separators, current collectors and battery tabs are important components related to the power performance, cyclic kinetics, and cycle life. This paper presents results on the surface modification and fabrication of separators, current collectors and laser welding of battery tabs.

Experimental

Coating of separators

Celgard 2500 of 25 μm thick was used as the separator for all coating development, cleaned in ethanol prior to coating experiments. Simple immersion coating of Celgard 2500 was conducted in five different solutions. 1) 1g of Polyvinylidene Fluoride (PVDF) in 180ml of acetone + SiO_2 of 0.02 μm particle diameter in 50% water colloidal suspension; 2) 1g of Polyvinylidene Fluoride-co-Hexafluoropropylene (PVDF-HFP) in 80ml of acetone + SiO_2 of 0.02 μm particle diameter in 50% water colloidal suspension; 3) 8ml of Tetraethyl orthosilicate (TEOS) in 100ml ethanol and 30ml DI water, with pH adjusted to 9 using ammonium hydroxide; 4) 8ml of Tetraethyl orthosilicate (TEOS) in

100ml ethanol and 30ml DI water + 1g PVDF, with pH adjusted to 9 using ammonium hydroxide; and 5) 8 ml TEOS in 100ml ethanol and 30 ml DI water + 1g PVDF-HFP solution, also with pH adjusted to 9 using ammonium hydroxide. All the chemicals of reagent grade were purchased from Aldrich. All the experiments were conducted in a beaker at 20 °C with continuous stirring.

Laser welding of battery tabs

An IPG Fiber laser YLR-500-SM was used in the experiments. The laser is a diode pumped single mode CW Ytterbium fiber laser operating at approximately 1,070 nm. The maximum output of the laser is 500W in a continuous wave (CW) mode with a $M^2 < 1.1$, randomly polarized and an output power stability of $\pm 2\%$. A Precitec Inc. laser welding head YW50 with a 200 mm focal length lens was used for welding. A CNC motion system was used to control the travel of the samples underneath the focused laser beam during processing.

Parameters were developed to produce lap joints with Ni-200 as the top material to a Ni coated mild steel because of their good electrical properties and corrosion resistance. As with all laser welding joint fit-up is very important to ensure good contact between the materials during welding. The laser power was set to 500W with focus located on the top surface of the Ni-200. Parameters were developed by welding 50.8 mm (2 inch) long sections. Various travel speeds ranging from 304.8 to 660.4 mm/min (12 to 26 inch/min) were then used to produce weld specimens for evaluation. The welds were then cross-sectioned, polished, etched and examined both optically and with SEM.

Fabrication of current collectors

Anode current collectors. Thin copper foil (99.9%, 18 μm -thick, All Foils Inc.) was used as a substrate for all of the porous-surfaced current collector development. For copper mesh diffusion bonding trials, commercially pure copper mesh (100 and 145 mesh, 55 μm -diameter wire) was purchased from Screen Technology Group Inc., while 200 mesh copper grid (99.99%, 55 μm -diameter wire) was provided by Anping Xindong Metal Wire Co. Copper Foil and mesh specimens were cut (20 mm x 20 mm) and stacked in pairs, i.e. grid on top of foil. These were then put between two ceramic plates to maintain close contact during the pre-bonding step, which was performed in a quartz tube inserted in a Lindberg 4''-diameter tubular resistance furnace. The pre-bonding heat treatment consisted in submitting the sandwiched materials to a heating cycle featuring a plateau of 2h @ 975°C under a flowing, re-purified argon atmosphere ($\sim 6 \times 10^{-9}$ ppm O_2) obtained by passing Ultra-High Purity argon gas (4 ppm O_2) through a Centorr Furnaces/Vacuum Industries Model 2A Gas Purifier. After cooling to room temperature, the pre-bonded samples were pressed under a load of 30 tons using an Enerpac, 100-ton hydraulic press. The pressed samples were finally diffusion-bonded by heating under conditions similar to those used for the pre-bonding step, but this time under a flow of 100% H_2 gas.

Cathode Current Collector. The starting materials used for cathode current collector is 1145 aluminum foil with 17 micron in thickness. The surface of the aluminum foil was modified through two different methods: 1) etching of aluminum through a photoresist mask, and 2) etching of aluminum foil through alumina mask produced by anodizing.

Etching of aluminum foil using a photoresist mask involves the steps of design and fabrication of a photomask, applying a thin film of photoresist to the surface of the aluminum foil by spinning, exposing and developing the photoresist film, and etching the aluminum to produce desired surface features; The procedures for another methodology, anodizing aluminum foil, include degreasing, annealing, anodizing, and pore enlargement treatment in phosphoric acid. After the surface modifications, the aluminum foil was characterized using various characterization tools, such as SEM and surface profiler.

Results & Discussion

Coating of separators

An important issue for battery performance and safety is related to the separator. Unexpected short-circuits across the separator induces hot spots where thermal runaway may breakout. Internal short-circuits are believed to occur either by protrusions on the electrode surface or by shrinkage of the separator upon heating. One way to prevent this from happening is to coat the thin and porous polymeric separator with ceramic coating.

SiO₂ ceramic coating was explored to increase the strength of the separator without sacrificing the ionic conductivity and cell performance. Five different methodologies were initiated as described in the Experimental section. Figure 1 shows the SEM morphology change of samples prepared from all five methodologies before and after coating. It can be clearly seen that all five methodologies successfully produced coatings on Celgard 2500. Furthermore, while the porosity of the substrate seems to be reduced in all cases, the porous feature of the surface is still maintained after coating. The right column of Figure 1 shows EDX (Energy Dispersive X-ray) Si mapping of the coated surfaces, which confirms the existence of Si which is reasonably related to SiO₂ because the simple immersion treatment is not expected to breakdown the SiO₂ particle suspended in the solution. It should be noted that further XPS analysis are needed for TEOS based solution to confirm the formation of SiO₂ even though the presence of Si is clearly shown in Figure 1.

Preliminary cyclic performance of cells using coated and uncoated separators was evaluated. Lithium ion coin cells were fabricated using coated Celgard 2500 as separators in a cell configuration of LiCoO₂ vs Li in 1M LiPF₆ 1:1 EC/DMC electrolyte. All the cells were cycled between 2.5V to 4.25V at a charge/discharge rate of 10mA/g. Figure 2 shows the capacity retention of a reference cell (a) and an example of cell (b) coated in PVDF-HFP + SiO₂. As can be seen, the capacity retention of coated sample is very consistent with the reference cell, indicating that the capacity retention performance is maintained using the separators with SiO₂ coating. It ought to be mentioned that for one particular cell an abnormal capacity increase was observed during the 23rd cycle with no obvious reason. Figure 3 shows the rate capability of a reference cell (a) and an example of cell (b) coated in PVDF-HFP + SiO₂. It is obvious that the charge/discharge rate capability of the cell is retained after coating of separators. This preliminary testing provides encouraging feedback for further development of selected methodologies to optimize the operating conditions and separator cyclic performance. In addition, no damage was observed on SiO₂ coated separators to date, but further research will be conducted upon completion of extended cycling using the coated separators.

Laser welding of tabs

Joining of battery leads and tabs forms the basis of the electrical connection between cells, current-collectors and cell-cans. The main considerations in joining of the battery leads and tabs are energy transfer capabilities, joint reliability and manufacturing costs. Laser welding is a non-contact process that produces high quality joints, excellent repeatability and offers some unique advantages over conventional welding processes since the high energy concentration of the laser beam reduces heat input to the joint, which is particularly promising for welding of thick battery tabs for on-board vehicular application. Battery tab materials can be nickel, aluminum, copper or a combination of these materials. However, these materials pose challenges in laser welding because of their high reflectivity. Furthermore, some joints require minimal heat input due to the joint location and the material thickness used [1].

This study investigated laser welding of 0.381 mm (0.015 inch) thick Ni-200 to 0.3175 mm (0.0125 inch) nickel-coated mild steel in a lap configuration. Figure 4 shows the top and bottom surfaces of welds produced at a travel speed of 457.2, 558.8 and 584.2 mm/min (18, 22 and 23 inch/min), respectively. As revealed by the photos of the bottom plates, full penetration welds were achieved at a travel speed of 457.2 and 558.8 mm/min, while the weld at 584.2 mm/min did not penetrate the bottom plate although discoloration was observed due to heating effect. SEM observation of the cross-sections of welds produced at 457.2 and 558.8 mm/min is shown in Figures 5. It is evident that the heat input between these two welds was at a threshold level that caused the welding mechanism to change from keyhole to conduction even though both welds are full penetration (Figure 6). The complete depth of penetration is represented by the solid line, while the dashed line showing the depth of nickel that penetrated into the mild steel plate. Once the welding mechanism becomes conduction mode (above 23 ipm) very little nickel is mixed into the mild steel plate. By examining the weld produced at 558.8 mm/min (Figure 5b), it is evident that the bottom layer of the nickel coating on the mild steel was melted indicating a full penetration weld. EDS mapping reveals that nickel is uniformly distributed throughout the complete fusion zone of the weld produced at 457.2 mm/min (Figure 7a), while the weld produced at 558.8 mm/min retains the nickel in the top portion of the fusion zone (Figure 7b) even though a full penetration weld was produced. The keyhole welding mode causes complete mixing of the nickel throughout the fusion zone, while conduction welding mode has very limited mixing effect for the nickel.

Fabrication and surface featuring of current collectors

Current collectors are important components in lithium-ion batteries. They support active materials in the electrode, and pass electrons between the active materials and the external circuits. Reducing the resistance between the active materials and the current collectors is beneficial to power performance of the lithium-ion batteries. Also, it is known that the detaching of the active materials from the current collectors during cycling contributes to reduced capacity of the battery [2]. In this study, new cathode and anode current collectors for lithium-ion batteries with low resistance and better active material retention are explored.

Anode Current Collector. Different current collector materials are presented in figures 8 to 10. The current collector produced using 200-mesh Cu grid can be observed

in Fig. 8a). As can be seen, the diffusion-bonding of the pressed Cu grid creates a regular array of slightly deformed square-shaped cavities ($\sim 60 \times 60 \mu\text{m}$). These depressions would be ideally suited to be filled with anode material and would permit increased contact between the active material and the current collector. The polished cross-section (Fig. 8b) also shows that the total thickness of the bonded porous over-layer is of the order of $45 \mu\text{m}$ (for a total collector thickness of $\sim 60\text{--}65 \mu\text{m}$) and that there is excellent bonding at the grid-foil interface.

In the case of the 145-mesh copper grid (Fig. 9a), a similar regular structure is obtained, but with larger cavities ($\sim 100 \mu\text{m}$ to a side). Naturally, the corresponding volume available to receive the active material is also larger. This is confirmed by the cross-section on Fig. 9b), where it is seen that the thickness of the grid material is also about $45 \mu\text{m}$. Once again, the diffusion bonding step created a large 'welded' interface between the grid segments and the copper foil, ensuring excellent charge and heat transfer from the grid to the foil substrate.

Using 100-mesh copper grid material resulted in the structure shown in figure 10a). The shape of the cavities is more regular in this case than in the previous two mesh sizes. The cavities are about $175 \mu\text{m}$ to a side by $40 \mu\text{m}$ deep (Figure 10b). This configuration would provide more space for active material, but less contact area to collect charge and extract heat from the inner part of the anode. On the cross-section (Fig. 10b), it seems that there is no contact between the grid and foil. However, this is only due to the fact that the grid has bonded to the foil mostly under the corners of the square cavities. More pressure would need to be applied to obtain a continuous bond between the grid and foil.

The different copper-current-collector configurations obtained thus far have not been optimized, but they show promise for use in lithium-ion batteries. Battery cyclic tests using the new anode current collectors will be conducted to evaluate their performance as battery components. Other grids and conditions (e.g. additional mesh sizes, different wire sizes, alternative processing parameters like compaction pressure and diffusion-bonding temperature, etc) could also be tested in order to optimize collector performance.

Cathode Current Collector. The surface profile of the sample etched using a photomask is shown in Figure 11. Grooves of about 3 microns in width and 3 microns in depth and 7 micron spacing were formed through etching the aluminum foil, indicating that the surface grooves with controlled dimensions can be produced with the use of the photomask. It can be easily calculated that the surface areas of the foil is increased by 60% through the formation of such etched grooves. These grooves are expected to reduce the electrical resistance between the active materials and the current collector, and to improve the retention of the active materials. The actual performance of the new current collectors will be verified through cycling test in lithium-ion batteries.

The surface morphology of the Al sample anodized in 0.4M phosphoric acid is shown in Figure 12. Shallow pores with a diameter of up to 2 microns and fairly even distributions were created on the surface of the aluminum foil. Some of the pores grew to about 4 microns after pore enlargement treatment. These results proved the feasibility of electrochemical etching. The size and distributions of the pores under various etching conditions will be further explored through the optimization of the process parameters for electrochemical etching and pore enlargement treatment.

Conclusions

1. SiO_2 coating of Celgard 2500 was successfully conducted using five different methodologies. Preliminary results showed the retention of porous surface and the cyclic performance with respects to capacity retention and charge/discharge rate capability.
2. Laser welding of battery tabs was proved to produce excellent surface finishes and no defects when joining Ni-200 to nickel-coated mild steel in a lap joint configuration for both full and partial penetration welds. Full penetration weld can be achieved at a maximum welding speed of 508 mm/min while a partial penetration at a maximum welding speed of 660.4 mm/min, using a 500W laser. The welding mechanism for full penetration welds changes from key hole to conduction mode at approximately 508 mm/min, affecting the percentage of nickel mixed into the fusion zone.
3. Anode current collectors featuring a porous over-layer of less than 50 μm thick diffusion-bonded to a thin (18 μm) copper foil were produced using Cu grids with three different mesh sizes. Regular structures with square-shaped cavities were obtained; Cathode current collector (Al foil) was modified through chemical etching using a photoresist mask, and electrochemical treatment in an aqueous phosphoric acid solution. The increased surface area will effectively benefit the retention of the active materials during cycling of the lithium-ion batteries as well as the charge transfer and heat extraction from the core of the electrodes.

Figure 1. Left column: Celgard 2500 before coating; middle column: Coated Celgard 2500; and right column: EDX mapping of Si

Figure 2. a) capacity retention of the reference cell using uncoated Celgard 2500; b) capacity retention of cell using Celgard 2500 coated in PVDF-HFP + SiO₂

Figure 3. a) rate capability of reference cell using uncoated Celgard 2500; b) rate capability of cell using Celgard 2500 coated in PVDF-HFP + SiO₂ solution.

(a) Top surface, 457.2 mm/min

(b) Bottom surface, 457.2 mm/min

(c) Top surface, 558.8 mm/min

(d) Bottom surface, 558.8 mm/min

(e) Top surface, 584.2 mm/min

(f) Bottom surface, 584.2 mm/min

Figure 4: Top and bottom surface of welds produced at 457.2 mm/min, 558.8 mm/min and 584.2 mm/min, 50X.

(a) Weld produced at 457.2 mm/min

(b) Weld produced at 558.8 mm/min

Figure 5: SEM observation of cross-sections of welds, (a) 457.2 mm/min, (b) 558.8 mm/min.

Figure 6: Depth of penetration (%) vs. travel speed (ipm)

(a) Weld produced at 457.2 mm/min

(b) Weld produced at 558.8 mm/min

Figure 7: EDS nickel mapping of welds, (a) 457.2 mm/min, (b) 558.8 mm/min.

8a)

8b)

Figure 8. Copper current collector with porous surface produced from 200-mesh Cu grid: a) SEM micrograph (60x); b) Optical micrograph, polished cross-section (200x).

9a)

9b)

Figure 9. Copper current collector with porous surface produced from 145 mesh Cu grid. a) SEM micrograph (60x); b) Optical micrograph, polished cross-section (200x).

10a)

10b)

Figure 10. Copper current collector with porous surface produced from 100 mesh Cu grid: a) SEM micrograph (60x); b) Optical micrograph, polished cross-section (100x).

Figure 11. Surface profile of Al sample etched using a photomask.

Figure 12. Surface pores created by anodizing in 0.4M phosphoric acid

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