Utilizing Sol-Gel Nano-composites to Improve the Safety and Reliability of Lithium-Ion Batteries

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Abstract
As a result of their lightweight and compact designs, lithium-ion batteries have emerged as the battery of choice for portable devices. However, short circuits in these batteries have been known to cause overheating and laptop fires or explosions. Much of this shorting can be attributed to the separator material that divides the electrodes of the battery.

In this paper, we display the potential of using nanomaterials in the form of sol-gels to improve the reliability of rechargeable batteries. In our experiment, polypropylene nonwoven fabric separators and experimental ethyl cellulose separators are coated with a thin layer of a sol-gel. Taking into consideration the highly insulative properties of sol-gels, these treated separators are then used to create a battery cell, utilizing sulfuric acid as an electrolyte to mimic a Li-ion battery. Subsequently, we test the voltage across a battery cell with the coated separator in several intervals over an extended period of time.

Through these experiments, it was conclude that all the treated separators on average performed better than or equal to the untreated separators.

1 Introduction

Nanotechnology, the science of manipulating matter on the nanometer (one billionth of a meter) scale holds enormous potential for affecting a diverse range of applications. Sol-gels are a promising class of nanomaterials characterized by a number of useful yet rare properties including extremely low thermal and electrical conductivity in addition to low weight [1]. The unique properties of sol-gels come as a result of the materials' nanostructure [2]. Sol-gels have become popular since they can take the form of a fiber, thin film, or monolithic structure, providing a broad range of applications [1].

One of the most promising applications of sol-gels lies in the electronics industry. With the recent increase in popularity of portable electronic devices, lithium ion batteries have emerged as the most common form of rechargeable battery. Given their minimal size and weight due to their high energy density, these batteries accounted for 63% of sales values worldwide in 2000 [3]. Despite these advantages, safety challenges remain due to the occurrences of laptop fires and explosions. Explosions result from the exothermic process that can be initiated when the cell shorts, due to a malfunction usually involving the separator. In the battery, the separator is a thin sheet of porous material that prevents the anode and cathode from having direct contact, while still allowing electrolyte to pass through. [4].

The ideal goal of improving the battery separator should contain a balance between a usable voltage and a long battery lifetime. While some coatings may insulate and protect the separator well, they can be too thick and not allow adequate electrolyte to flow through. This renders a battery inefficient as its voltage is much lower. Other coatings allow for a consistently high voltage, but do not protect the separator, which ultimately leads to a shorter battery life.

However, films formed from sol-gels possess the potential to improve the performance of laptop batteries in both of these aspects. As excellent insulators, they may make rechargeable lithium-ion batteries safer and more environmentally friendly by reducing the amount of heat that emanates from each battery [5]. They have the potential to improve the performance of batteries since their pores promote "improvement in the ionic transport at the electrode/electrolyte interface" [5]. The thin dimensions of the sol-gel coating, made possible by the nanometer-scaled particles, do not hinder the passage of electrolyte or voltage. Perhaps most beneficial, they would be relevant to the consumer because they could yield even-smaller laptop batteries [6].

This study aims to utilize the sol-gel process to produce a uniform coating material for a lithium ion battery separator. Optimally, this coating will provide the separator with increased thermal and electrical insulation. In addition to this, the sol-gel coating adds an additional layer of strength thereby reducing the chance of the membrane becoming punctured. The effectiveness of our coating will be measured through its voltage. These improvements combined will make for a more efficient and safer lithium ion battery.

2 Background

2.1 Lithium Ion Batteries

Lithium ion batteries have generated large amounts of interest due to their high energy density-to-size ratio, as seen in Fig. 1.1. This property makes Li-ion batteries especially advantageous to portable electronics manufacturers, in comparison to other common batteries such as lead-acid and nickel-cadmium. These differences aside, the basic structure of a Li-ion battery is very much similar to traditional battery cells, which are composed of five main components. An anode and cathode, which are negative and positive respectively, lie on opposite ends of the battery cell. Between these two electrodes an electrolyte fluid containing a large number of electrons can flow. A separator usually divides the cell in half, preventing the flow of electrons to the anode. The insulation of the anode from the cathode is necessary to prevent electrons from flowing directly through the electrodes, which would cause a short circuit. Therefore, the quality of the separator can determine the reliability of the battery. Coatings of certain treatments, such as sol-gels, have the potential to improve the separator's quality.

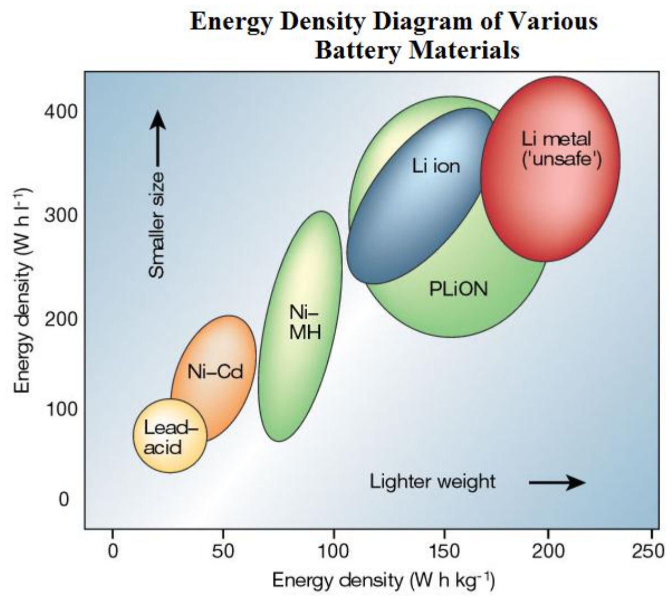

Figure 1- Graph displaying the energy density of commonly used battery types. Lithium ion batteries display excellent energy density while remaining small and light weight [3].

2.2 Properties of Sol-Gels

The sol-gel process is a method of linking nanometer sized precursors in a solution or colloid to form a polymer when deposited. Regardless of the precursor material utilized in the formation of the sol-gel, the material always shares the nano-pores that are characteristic of sol-gel materials. These air containing pores contribute to sol-gels' high thermal and electrical insulator properties, similar to the structure of many lightweight insulating foams. The sol-gel's weight and insulative properties make it especially applicable to improving batteries.

Moreover, a major benefit of the sol gel process is its ability to operate without expensive machinery in short periods of time. Combined with the low cost of the materials necessary to produce a sol-gel, this advantage makes the sol-gel process an alluring medium for varied applications such as lithium ion batteries.

2.3 Sol-Gel Process

Two processes can be utilized in the formation of a sol gel; the first, which is utilized in this study, begins with a colloidal suspension of silica. The second sol-gel process utilizes an alkoxide solution as a precursor material. A colloid is a substance in which numerous suspended particles are small enough that they do not settle out of the liquid after a given amount of time, but are still large enough that the particles do not dissolve. This suspension of nano-sized silicon particles becomes usable after drying at room temperature for a short time. During this time, the nanoparticles aggregate to form a highly porous solid, key to the sol-gel structure.

The colloidal process has numerous advantages over its alternative, the alkoxide solution method. Although the alkoxide is more capable of producing a uniform solid, it requires more advanced equipment to create. In addition to this, the curing process for alkoxide solutions is considerably longer than that of colloidal sol gels.

2.4 Current Uses of Sol Gels

Given their wide range of properties, sol gel applications have been utilized in many industries. Because they are simultaneously lightweight and strong, sol gels have been widely used in improving ceramics. Their small individual particle size also makes them applicable to use in agriculture as herbicides and in biomedicine.

While nanotechnology has been previously applied in the electrodes of the battery to improve their performance, the sol gel process specifically has not been utilized as a method to coat and treat the separator.

3 Method

Sol gels were formed by pouring Ludox, a commercial colloidal silica product, into two Petri dishes and mixing in NaCl solutions. The presence of NaCl ions disrupted the suspended colloid particles, causing sol particles to aggregate into a gel. First, three separate Petri dishes were filled with 30 mL of Ludox. .50M, 2.0M, and 0.25M NaCl solutions were then added and incorporated into the first, second, and third dishes respectively. The different concentrations of NaCl were designed to change the time it would take for the gel to form, which would subsequently affect the thickness and uniformity of the coatings. Once all clumps of NaCl were no longer visible, the Ludox-NaCl mixtures were each applied to two different types of separators: a 65% cellulose/35% ethyl cellulose separator and a polypropylene battery membrane. These two types of separators were chosen because they are current standards. From there, the gels and membranes were ultimately allowed to dry at room temperature to ensure a simple and cost effective method that may be appealing for industrial purposes.

Once the membranes and sol gels had dried, they were tested for thermal and electric conductivity. Thermal conductivity was measured by recording the amount of time needed for the temperature reading on a thermometer in hot water to increase 10°C. First, this time was measured when the thermometer was placed directly into the hot water. Afterwards, the thermometer was placed into a plastic bag along with sol gel fragments. Again, the time for the temperature to increase 10°C was measured.

Then, electric conductivity was measured with a multimeter based on the voltage across the two terminals of a 1.5V Duracell AA battery. Then, one by one, each membrane was placed on either terminal of the battery and the voltage was measured again. This test was to ensure that the sol-gel coating had not adversely affected the separator. A measurement of 0.0 volts would indicate that the separator was an effective insulator, while any positive reading would indicate the unwanted flow of electrons.

To test the effect of the treated battery separators, simulation open laptop batteries were created. To do this, the bottoms of six glass slides were painted with a paste of 0.9978 g graphite (carbon black) in 10 mL of deionized water. Likewise, to create cathodes, the tops of the same slides were painted with 5.1666 g manganese dioxide in 5 mL of deionized water. Carbon black and manganese dioxide were chosen as the electrode materials for because they mimic current battery models and therefore would allow us to keep these factors constant. These slides were then assembled into cells and tested with the voltmeter; it was found that none of the cells had short circuits or produced a voltage. It was concluded that the separator did not allow any electron transfer, so it exhibited the desired behavior.

Afterwards, 1M sulfuric acid was added to supply H+ ions for the batteries' redox reactions to simulate a Li-ion battery. Using a multimeter, open voltage readings were taken immediately after the acid was added and later at ten-minute intervals. Each time, 30 seconds elapsed after the multimeter had been connected to the wires before voltages were recorded.

Additionally, two control batteries, one with a cellulose separator and the other with a polypropylene separator, were made. They did not receive any Ludox or NaCl solution.

Results

The thermal conductivity data confirms that sol gels are insulators. Without any insulator, the temperature reading took an average of 4.92 seconds to increase by 10°C. 2 M NaCl solution along with Ludox increased this time to 2:23:10, while 0.5M NaCl increased it to 1:00:14. In comparison, bubble wrap increased this time to 1:02:52.

The dried polypropylene membranes remained crisp and were coated evenly. The cellulose membranes, on the other hand, wrinkled up and were not coated evenly.

Voltage Output of a Battery Utilizing Different Separator Materials

Voltages (mV)				
Time (min.)	0.25 M Poly.	0.25M, Cellu.	0.50M, Poly.	0.50M, Cellu.
0	22.2	8.8	21.0	2.8
10	9.2	39.0	11.7	37.6
20	3.7	36.1	4.4	11.6
30	3.7	18.3	14.9	11.2
40	16.8	8.6	5.5	19.7
50	15.2	15.2	11.1	20.3
60	15.3	9.7	28.4	22.5

Voltages (mV)				
Time (min.)	2.0M, Poly.	2.0M, Cellu.	Cellu. (Control)	Poly. (Control)
0	23.4	12.4	N/A	N/A
10	41.8	15.9	N/A	N/A
20	14.9	15.9	N/A	N/A
30	30.5	85.9	58.8	N/A
40	25.7	196.4	6.5	5.5
50	5.9	204.0	34.7	11.7
60	11.4	261.6	3.5	21.6

Trial Two Voltages (mV)				
Time (min)	.25 M Unwov. Poly	.25 M Cellu	.5 M Unwov. Poly	.5 M Cellu
10	6.4	10.5	4.3	9.9
20	21.5	9.8	2.7	24.2
30	6.5	6.8	1.8	7.5
40	8	7.9	4.3	8.6
50	6.8	5.4	8.8	4.2
60	8.9	3.1	5.7	7.3
Time (min)	2 M Unwov. Poly	2 M Cellu	Poly. Control	Cellu. Control
10	8	8.7	6.7	2.6
20	3.8	3.8	4.4	3.8
30	4.3	7.1	6.2	17.5
40	2.5	5.8	8.7	2.0
50	5.7	9.6	4.1	1.9
60	4.2	6.5	6.8	6.9

Table 1- Voltage output by the sulfuric acid battery with various separator membranes

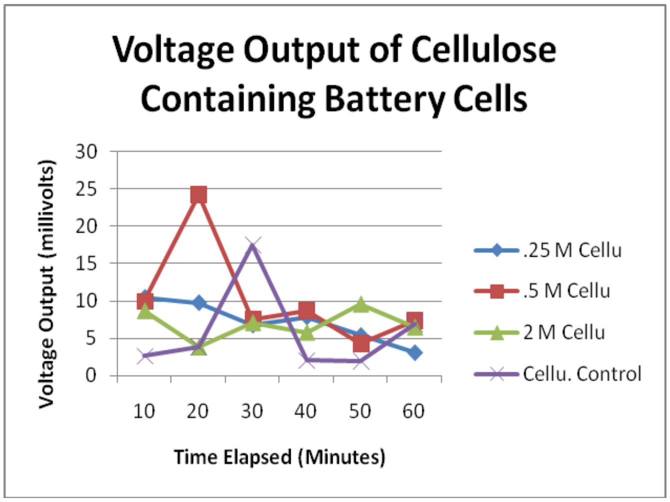

Figure 2- Graphical representation of voltage output of the cellulose battery membranes. Increased molarity of the membrane resulted in higher voltage output

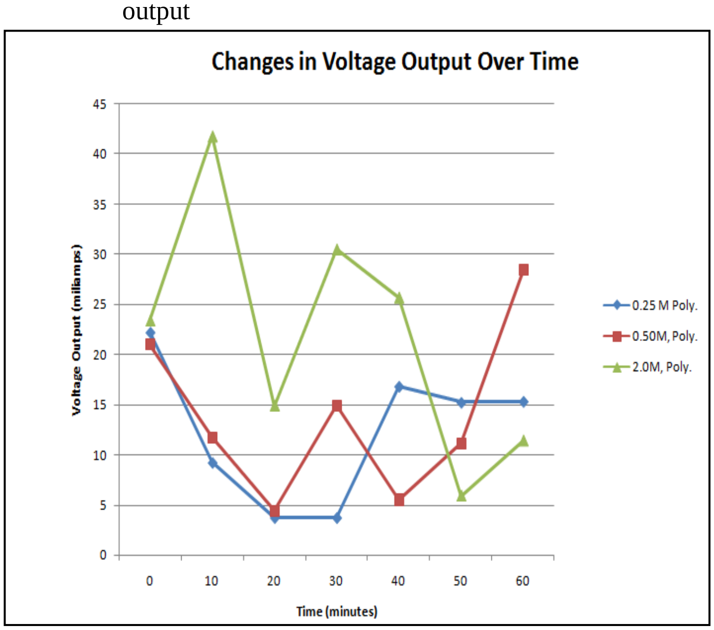

Figure 3- Graphical representation of voltage output of the trial one data for polypropylene membranes.

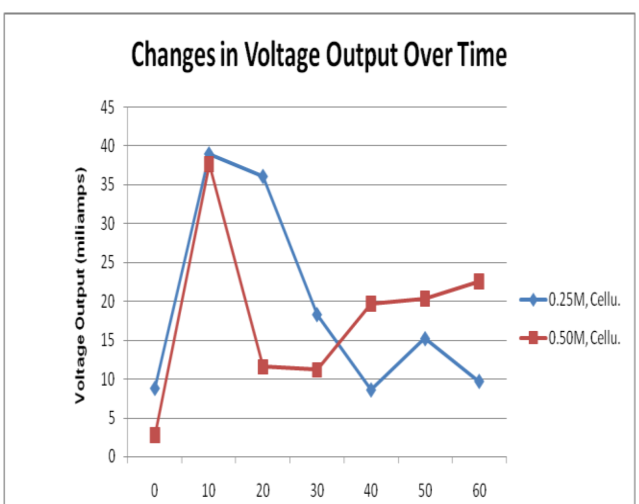

Figure 4- Graphical representation of voltage output of the trial one data for the cellulose membranes.

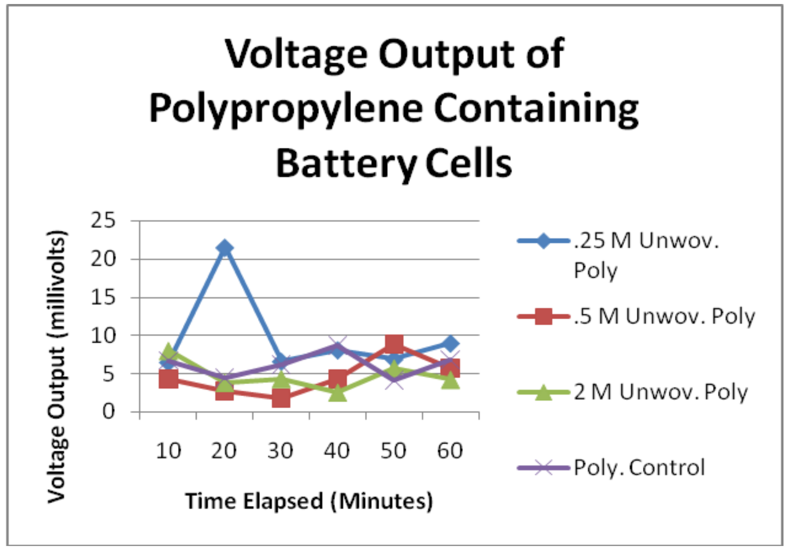

Figure 5- Graphical representation of voltage output of the trial one data.

Preliminary testing showed that none of the coated membranes allowed for voltage to pass through and thus were fully effective electrical insulators. All of the coatings produced increased the amount of voltage output by the battery relative to the control samples.

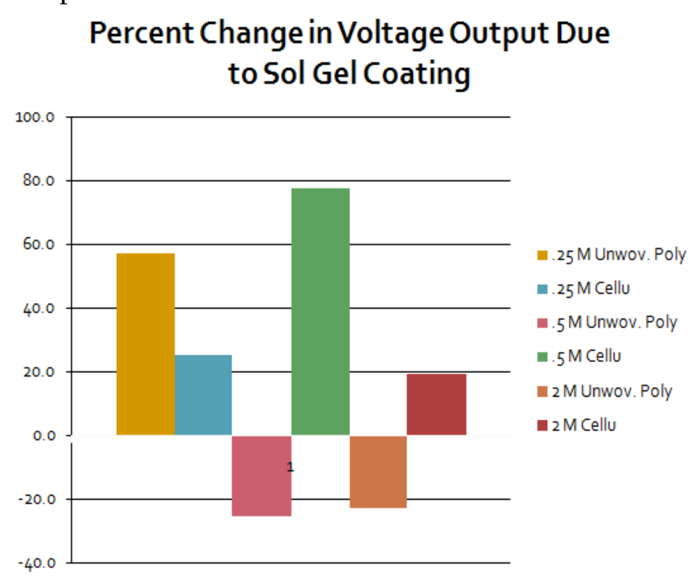

Figure 6- Graphical representation of percent change in voltage of different sol-gel coatings. The majority of samples tested outperformed industry standards

It was found that, generally, an increased concentration of NaCl solution added to the Ludox before gelling caused different outcomes depending on the material that was coated. With the unwoven polypropylene battery separator, an increase in

NaCl resulted in a decrease in total voltage output. The opposite was found to be true for the cellulose ethyl-cellulose membrane until the two molar concentration. At this level, it was hypothesized that the increased thickness from the sol-gel coating was preventing effective electrolyte flow through the battery.

Overall, most coatings resulted in a net increase in voltage output and sustain their output. Polypropylene coated membranes, while not able to output as much voltage as cellulose membranes, were able to sustain consitant outputs. Cellulose ethyl-cellulose membranes output high voltages; however, after testing it was found that some of the cathode had been reduced suggesting that the life of the battery would be less than that of the polypropylene containing battery.

Related Work

Nanotechnology in Li-ion Battery Improvement

Due to their unique properties, nanomaterials have previously been tested as alternatives to various components of lithium-ion rechargeable batteries, aside from the separator.

In 2007, previous research identified the major advantages of replacing the typical graphite anode with one of silicon nanowires. Due to silicon's high electrical capacity as well as the nanowire's small diameter, the battery is able to hold a greater capacity of charge while the anode only shirks and expands a negligible amount [7]. This additionally contributes to the longevity of the battery by preventing fractures of the anode. Unlike our experiment which focused on the separator material, these researchers worked to improve the anode.

Furthermore, researchers have applied carbon nanotube technology for the electrodes of the battery cells. In previous research, the carbon nanotubes were enhanced with cellulose, creating a flexible battery. While the nanotubes served as electrodes, the cellulose became the separator [3]. Although this method used nanotechnology, it did not specifically use the sol-gel process as we did.

Adjustments to the Separator In trying to improve the safety of batteries, many researchers have studied and modified the properties of the separator, recognizing its critical role in battery performance. The importance of a reliable separator becomes especially significant in larger lithium-ion batteries, such as those used in hybrid and electric vehicles.

Because of their lightweight property, car manufacturers are especially interested in applying lithium-ion batteries to these types of cars. Recent industrial research has developed a safer lithium-ion separator that may be usable in cars. The special polymer film is based on an advanced co-extrusion technology and has a higher thermal stability [8, 9]

Conclusion

We observed that both the changes in the molarity of sodium chloride solution added to the Ludox and the separator material that is coated affect the voltage output of the cell in which they are incorporated. It was found that, generally, the cellulose and ethyl-cellulose separator membrane outputted a greater voltage than the polypropylene separators. Therefore, the cellulose separator would likely be best suited for implementation into a commercial battery.

During the coating process, it was noted that the dried polypropylene membranes remained crisp and were coated evenly. The cellulose membranes, on the other hand, wrinkled up and were not coated evenly. For all membranes, greater NaCl concentration led to more flakes. Nevertheless, flakes were more visible on the cellulose membranes. This is important to note should the membranes become incorporated into a commercially available product.

Sol gels may soon become essential in electronics. They are superb insulators especially when their low cost is taken into account. It was found that the sol-gel process is about 48% cheaper than currently used battery separators.

This research provides strong evidence for the prospect of utilizing sol-gel nanotechnology as a cost effective process for producing battery separators.

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References

1. L. Klein. Processing of nanostructured sol-gel materials. *Nanomaterials: Synthesis, Properties and Applications* 147-164 (1998).
2. S. Sumio. *Handbook of Sol-Gel Science and Technology.* (2004).
3. J.-M. Tarascon, M. Armand. Issues and challenges facing rechargeable lithium batteries. *Nature* **414**, 359-367 (2001).
4. J. Cho. Improved thermal stability of $LiCO_2$ by nanoparticle $AlPO_4$ coating with respect to spinel $Li_{1.05}Mn_{1.95}O_4$. *Electrochemistry Communications* **5** 146-148 (2003).
5. C. Fonseca. Electrochemical properties of a biodegradable polymer electrolyte applied to a rechargeable lithium battery. *Journal of Power Sources* **159,** 712-716 (2006)
6. Y. Rho, Kiyoshi Kanamura. Fabrication of thin film electrodes for all solid state rechargeable lithium batteries. *Journal of Electroanalytical Chemistry* **559** 69-75 (2003).
7.D. Stober. Nanowire battery can hold 10 times the charge of existing lithium-ion battery. *Stanford Report* (2009).
8. J. Neu. ExxonMobil chemical announces new developmental grades of battery separator film for safer lithium ion batteries. *Reuters* (2009).
9. S. Christiansen. Power of technology makes future a reality. *The Lamp* 3-5 (2009).