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Methods of coating a three-dimensional structure with polymer electrolytes for lithium-ion batteries

Abstract. *The paper considers various methods of conformal coating the three-dimensional structure of Ni foam with polymers as electrolytes in lithium-ion batteries. Polymethylmethacrylate (PMMA), polyacrylonitrile (PAN), polyvinylidene fluoride (PVDF), and polyethylene oxide (PEO) were chosen as polymer electrolytes because of their good ionic conductivity and mechanical stability. Conformal coating was performed using two methods: drop coating, dip coating. The polymer-coated three-dimensional Ni foams were characterized by field-emission scanning electron microscopy (FE-SEM) to determine the more conformal coating method and testing the ionic conductivity of polymers. From this research, it could be concluded that the dip coating method allows a more conformal coating of the three-dimensional Ni foam structure and the polymers obtained by this method have a good value of ionic conductivity.*

Keywords: *coating, electrolyte, polymer films, ionic conductivity, polymethylmethacrylate, polyacrylonitrile, polyvinylidene fluoride, polyethylene oxide.*

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Introduction

Rechargeable lithium-ion batteries are currently the optimal portable source of electricity. There is an increasing number of new materials that are being explored as the cathode and the anode annually. The electrodes are separated by a polymer separator and a liquid organic electrolyte with dissolved salt. However, these organic solvents could ignite upon mechanical impact or short circuit, also they may react with electrode materials [1].

As the solution to this, researchers are turning to lithium ion-polymer technology, where the polymer acts as a polymer electrolyte and separator. Ion-conducting polymers are used as polymers, which replace the traditional porous separator and liquid electrolyte. This improves battery safety because polymer electrolytes are not flammable and also these polymers are able to provide thinner battery cells [2].

In modern mobile technology (such as smartphones, laptops, digital cameras and etc.) the use of polymer electrolytes has important advantages over liquid electrolytes, such as: high energy density, flexible shape, light weight, and less chance for electrolyte leakage [3].

Polymethyl methacrylate (PMMA) [4,5], polyacrylonitrile (PAN) [6,7], polyvinylidene fluoride (PVDF) [8,9], and polyethylene oxide (PEO) [10-12] were chosen as polymers because they have good ionic conductivity and mechanical stability, that are studied extensively by other researches.) Polymer electrolyte production methods: drop coating, dip coating. The aim of the study was to prepare a polymer electrolyte for lithium-ion batteries with 3D structure and to check their ionic conductivity. The objective was to obtain conformal coating of polymer electrolyte on Ni foam with a good ionic conductivity value.

Experimental part

2.1 Materials

Polymers are PMMA (Mw 100,000; Sigma Aldrich); PEO (Mw 100,000; Sigma Aldrich); PAN (Mw 150,000; Sigma Aldrich); PVDF (Mw ~534,000; Sigma Aldrich); Ni foam (99.5% purity, 0.9 mm thickness, Good Fellow); solvents are acetonitrile (ACN, Sigma Aldrich) and N,N-dimethylformamide (DMF, Sigma Aldrich).

2.2 Drop coating and dip coating methods

To obtain conformal polymer electrolyte coating on Ni foam, the polymers were dissolved in the following solvents: PMMA and PEO in acetonitrile (ACN), PAN and PVDF in N,N-dimethylformamide (DMF). Following polymer solutions were prepared: 2% PMMA in ACN, 2% PEO in ACN; 2% PAN in DMF, 2% PVDF in DMF. The polymer solutions were stirred continuously with a magnetic stirrer for several hours at room temperature to ensure complete dissolution.

After that, the polymer solutions were applied on the surface of the Ni foam by drop coating and dip coating methods. After coating the Ni foam with the polymer, ~~the~~ samples were dried in a vacuum oven for 1 hour at 60°C. To obtain multilayer films, the Ni foam was immersed in the polymer solution for 10 minutes and then dried in a vacuum. Then it was immersed again in the polymer solution and dried again. This procedure was repeated four times.

2.3 Characterization

Morphological feature of the electrolytes obtained by both methods was observed by Scanning Electron Microscope (SEM, Crossbeam 540). The distribution of chemical elements in the obtained electrolyte films was identified by EDS (SEM, Crossbeam 540). The ionic conductivity was measured using an electrochemical impedance analyzer (Metrohm Autolab).

Result and Discussion

After the polymer electrolytes PMMA, PEO, PAN, PVDF were applied to Ni foam, the morphological characteristics of these films as well as elemental analysis were investigated. SEM images show that drop coating and dip coating methods allow to obtain polymer films of PMMA, PEO, PAN and PVDF of different thicknesses with a smooth and homogeneous structure.

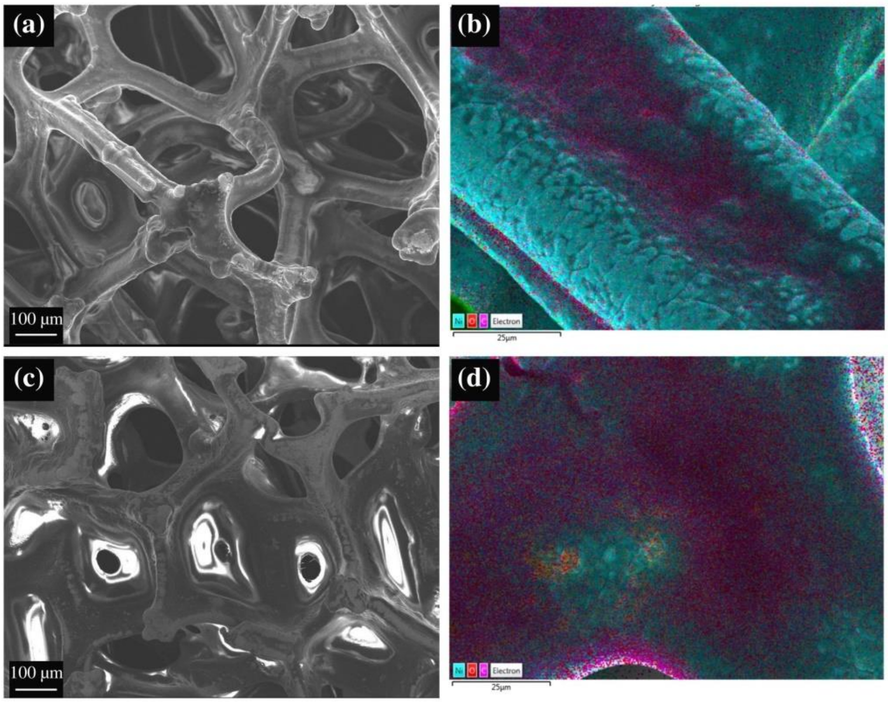

Fig. 1. SEM images of Ni foam coated with PMMA film by methods: (a) - drop coating; (c) - dip coating. Elemental analysis of PMMA film on Ni foam obtained by methods: (b) - drop coating; (d) - dip coating

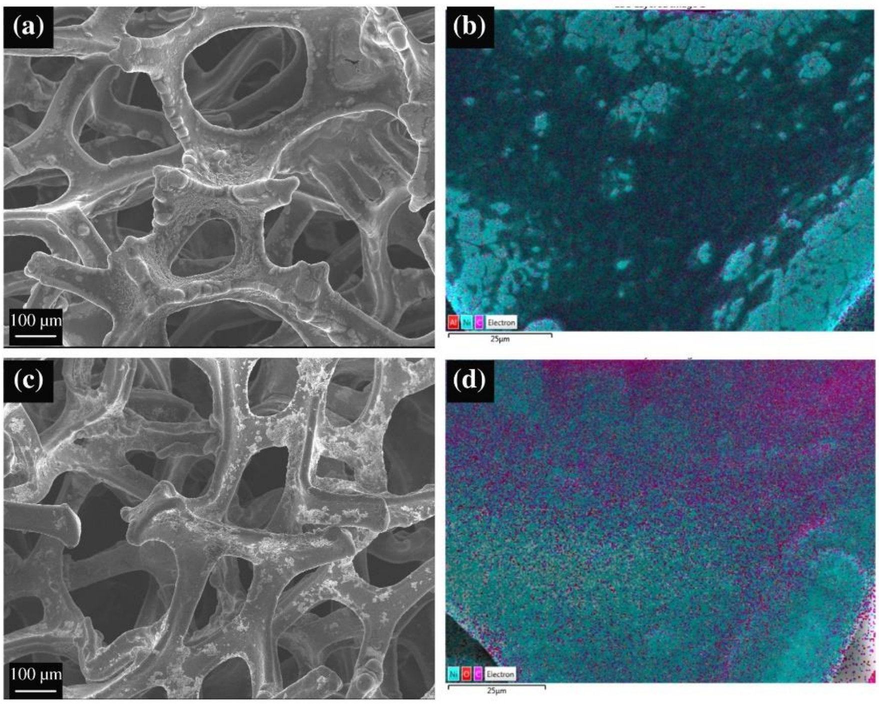

Fig. 2. SEM images of Ni foam coated with PEO film by methods: (a) - drop coating; (c) - dip coating. Elemental analysis of PMMA film on Ni foam obtained by methods: (b) - drop coating; (d) - dip coating

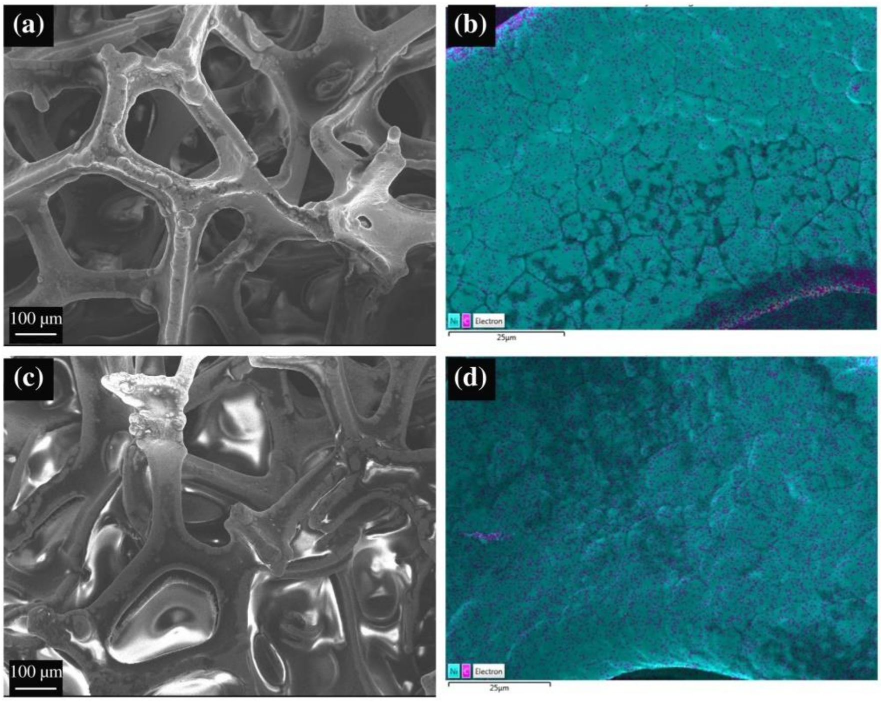

Fig. 3. SEM images of Ni foam coated with PAN film by methods: (a) - drop coating; (c) - dip coating. Elemental analysis of PMMA film on Ni foam obtained by methods: (b) - drop coating; (d) - dip coating

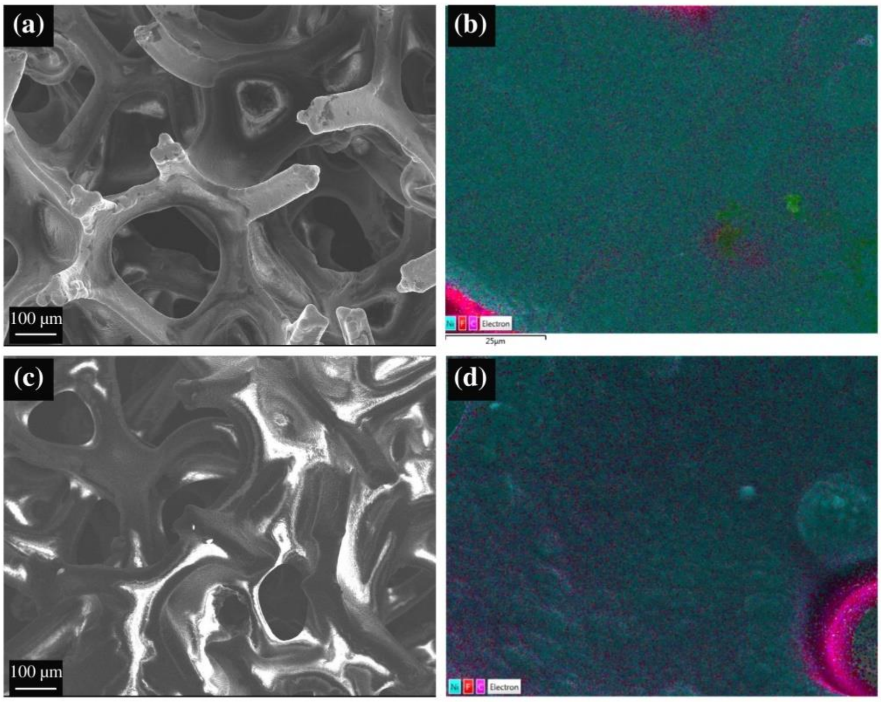

Fig. 4. SEM images of Ni foam coated with PVDF film by methods: (a) - drop coating; (c) - dip coating. Elemental analysis of PMMA film on Ni foam obtained by methods: (b) - drop coating; (d) - dip coating

The SEM images clearly show that the Ni foams with polymer electrolytes obtained by the drop coating method (Fig. 1,2,3,4 (a)) are partially covered by a polymer layer, which is also confirmed by the elemental analysis of the samples (Fig. 1,2,3,4 (b)). However, the Ni foams with polymer electrolytes obtained by dip coating (Fig. 1,3,4 (c)), on the contrary, have a conformal coating of the three-dimensional Ni foam structure. The film microstructures look very dense. The polymer films' surface morphology appears to be uniform, dense and smooth. EDS analysis also confirms this (Fig. 1,3,4 (d)). The PEO polymer in Fig. 2 (c,d) has a partial coating, presumably because PEO has a high solubility in these solvents. Therefore, the PEO samples have a weak partial film coating. Having compared the two methods, it can be said that the polymer films obtained by dip coating method allow conformal coating of 3D structure both outside and inside, in contrast to the method of drop coating.

Polymer electrolytes for lithium ion batteries must have good ionic conductivity. Ionic conductivity is strongly related to the charge density and mobility of the active spices [13]. Ionic conductivity depends on the crystallinity of the polymer electrolytes; the higher the crystallinity, the worse the ionic conductivity of the polymer will be. Samples obtained by dip coating were tested for ionic conductivity. A solution of $LiPF_6$ lithium salt in a 1:1 (v/v) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) was added to the polymer electrolytes to reduce polymer crystallinity and the ability to conduct lithium ions. The ionic conductivity of the obtained polymer electrolytes was measured by sandwiching the samples between two steel blocking electrodes (stainless steel (SS)). To evaluate Li conductivity of the obtained polymer electrolytes, the ac impedance was measured on a SS/polymer+Li salt/SS cell. Figure 5 shows Nyquist plots of PMMA, PAN, PEO, PVDF polymer films at ambient. Ionic conductivity is calculated based on Eqn. 1:

$$\sigma = \frac{l}{R_p \cdot S} \qquad (1)$$

where, σ - ionic conductivity, *l* - film thickness, R_p - bulk resistance, S - area of the electrode. The results of ionic conductivity of the obtained polymer electrolytes are shown in Table 1.

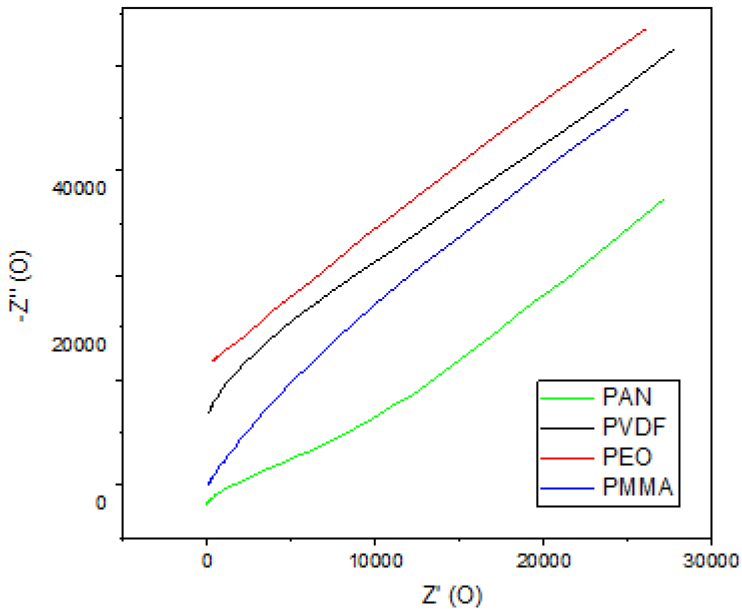

Fig. 5. Nyquist plots of polymer electrolytes on stainless steels at ambient

Table 1

Ionic conductivity of polymer electrolytes obtained by dip coating

Values	PMMA	PAN	PEO	PVDF
Rp	194,69 Ω	5913,6 Ω	1077,1 Ω	7711,9 Ω
S	1,1586 cm^2	1,1586 cm^2	1,1586 cm^2	1,1586 cm^2
l	0,026 cm	0,011 cm	0,013 cm	0,012 cm
σ	**1,1526*10^{-4}**	**1,6054*10^{-6}**	**1,0417*10^{-5}**	**1,3430*10^{-6}**

The PMMA polymer film offers the highest conductivity of 1,1526*10^{-4} S $см^{-1}$. The thickness of polymer films is given in Table 1. Charge transport requires both efficient ion dissolution and a low migration barrier. Consequently, the solvation mobility of Li^+ ions must be optimized through the polymer matrix to produce superionic polymer electrolyte thin films, which requires the amorphous nature of the polymer electrolyte matrix [13].

Conclusion

In this study, we prepared polymer electrolytes PMMA, PEO, PAN, and PVDF by drop coating and dip coating methods. The polymer electrolytes were deposited on a three-dimensional Ni foam structure. A more complete confomal coating was obtained by PMMA, PAN, and PVDF polymers by the dip coating method, as confirmed by SEM and EDS results. PEO polymer electrolyte has high solubility, experiments with other solvents should be conducted to obtain ~~a~~ more conformal coating. The layer by layer technique allows you to get ~~a~~ the conformal coating of a three-dimensional structure. The ionic conductivities of polymer electrolytes were checked. Polymers have good ionic conductivity at room temperature, PMMA film showing the highest value. Further experiments are planned with the addition of lithium salt and plasticizers to the polymer composition in order to improve the ionic conductivity of the polymer electrolytes and battery cell assembly.

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Литий-ионды аккумуляторларға арналған полимерлі электролиттермен үш өлшемді құрылымды жабу әдістері

Аннотация. Мақалада литий-ионды аккумуляторларындағы электролиттер ретінде полимерлермен никель көбігінің үш өлшемді құрылымын конформды жабудың әр түрлі әдістері қарастырылған. Полимерлі электролиттер ретінде полиметилметакрилат ПММА), полиакрилонитрил (ПАН), поливинилиден фторид (ПВДФ), полиэтилен оксиді (ПЭО) таңдалды. Өйткені олар жақсы ион өткізгіштігі мен механикалық тұрақтылығына ие. Конформды жабу екі әдіспен жүзеге асырылды: тамшылатып жабу, батыру. Полимерлермен қапталған 3D никель көбіктері полимерлердің ыңғайлы жабу әдісін анықтау және иондық өткізгіштігін тексеру үшін өрістерді сканерлейтін электронды микроскопиямен (FE-SEM) сипатталды. Осы зерттеу нәтижесінде батыру әдісі никель көбігінің үш өлшемді құрылымын неғұрлым жайлы жабуға мүмкіндік береді. Осы әдіспен алынған полимерлер жақсы ион өткізгіштікке ие болады деген қорытынды жасауға болады.

Түйін сөздер: электролит, полимерлі қабықшалар, иондық өткізгіштік, полиметилметакрилат, полиакрилонитрил, поливинилиден фторид, полиэтилен оксиді.

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Методы покрытия трехмерной структуры полимерными электролитами для литий-ионных батарей

Аннотация. В статье рассмотрены различные методы конформного покрытия трехмерной структуры пены никеля полимерами в качестве электролитов в литий-ионных батареях. В качестве полимерных электролитов выбраны полиметилметакрилат (ПММА), полиакрилонитрил (ПАН), поливинилиденфторид (ПВДФ), полиэтиленоксид (ПЭО), так как они обладают хорошей ионной проводимостью и механической стабильностью. Конформное покрытие осуществлялось с помощью двух методов: капельное покрытие, погружение. Покрытые полимерами трехмерные пены никеля были охарактеризованы полево-эмиссионной сканирующей электронной микроскопией (ФЭ-СЭМ) и инфракрасной спектроскопией преобразования Фурье (ИК-Фурье) для определения более конфорного метода покрытия и проверки ионной проводимости полимеров. Из данного исследования можно сделать вывод, что метод погружения позволяет более конформно покрыть трехмерную структуру пены никеля и полученные данным методом полимеры имеют хорошее значение ионопроводимости.

Ключевые слова: покрытие, электролит, полимерные пленки, ионная проводимость, полиметилметакрилат, полиакрилонитрил, поливинилиденфторид, полиэтиленоксид.

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