

ELECTRODE MATERIALS FOR LI-ION BATTERIES BASED ON DIATOMITE

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Abstract

Energy is a fascinating field that has been developing rapidly for many years. Various articles about alternative energy sources, batteries, and supercapacitors are being published today. This article is about the lithium-ion battery. The batteries come with three specific parts, one of which is the anode. In this area, electrons accumulate, which provide power to electrical devices. Since 2011, graphite anodes have been most commonly used in lithium batteries. Silicon is a tempting proposition for scientists working on next-generation lithium batteries with the potential to hold many times more energy than graphite. Silicon is a promising material for the anodes of lithium-ion batteries of a new generation since, in the process of electrochemical introduction, it can accumulate a large amount of lithium (up to 4.4 Li atoms per Si atom) and provide very high values of specific capacity (4200 mAh/g). The present article overviews the prospects for using diatomaceous earth (DE) (from the Mugalzhar region) in the continuous expansion of energy science and technology. Environmentally friendly silicon dioxide and silicon production, diatomaceous earth has the necessary nano-microstructure, which offers the advantages inherent in existing and new applications in electrochemistry, catalysis, optoelectronics, and biomedical engineering. Silicon, silicon, and silicon-based materials are useful for energy storage and storage applications. Also, for comparison, the surface of the DE was modified with nanotubes. The electrode material has been characterized by EDAX, SEM, BET, and electrochemical techniques. The results obtained showed the advantage of modified diatomite (specific surface area – 188.9 m²/g and particular capacity of the battery – 120 mA·h·g⁻¹) compared to unmodified (specific surface area – 39.1 m²/g and a particular degree of the battery – 100 mA·h·g⁻¹).

Keywords: diatomite, CNTs, electrochemical electrode, batteries.

1. Introduction

Most natural materials have a large, hierarchical organization, which remains an area of great interest to researchers today. One such naturally occurring material is DE, formed after forming cell walls of amorphous silica cells of dead diatoms in marine sediments. Diatomite, also known as diatomite, was initially discovered in 1836 by German farmer Peter Casten and has long been mined in about 30 countries. DE is characterized by unique properties such as high porosity, lightweight, small particle size and high surface area, chemical inertness, and low thermal conductivity, thus paving the way for many applications. It is usually like a pale powder. The typical particle size range reported for DE

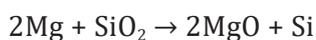
is approximately 10–200 μm. Regardless of the source of diatomite, SiO₂ is present as the main phase. Other phases in DE: CaO, MgO, Fe₂O₃ and Al₂O₃ [1].

The use of diatomaceous earth began 2000 years ago. Reports show that the Greeks used diatoms in ceramics and bricks [2]. Typically, DE additives are found as filter aids, functional additives, absorbents [3], natural insecticides, and materials for soil improvement. Recently, diatomite has received considerable attention in the scientific community. DE offers a unique way to imitate nature by using it as a template and precursor for materials with the necessary nanostructures. Most of today's materials are expected to have nano-micro structures to meet the multiple functionalities of specific applications. Materials

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that exhibit the required properties at the macro scale are often subject to failures due to chemical, thermal, electronic, or mechanical processes at the nano and micro scales. An outstanding example is a possibility of using silicon as an anode material in lithium-ion batteries. This area is well explored, continues to be explored, and remains a potential game changer in battery technology. It is known that the theoretical capacity of silicon is higher than graphite [1].

The focus on diatomite earth has yielded many interesting results, based on which excellent research has been reported on the use of diatomaceous earth in energy conservation [4-16]. In [4-10] magnesiothermic method of diatomite is used to obtain pure silicon by the equation



and its application as an anode. Electrochemical evaluation indicates that the diatomaceous earth could be a promising precursor of porous silicon anode material. The composite electrode using diatomite was manufactured by pyrolysis methods [11], electrostatic spinning technology [13]. In [12] study, a composite separator was prepared by coating a diatomite/polyvinylidene fluoride (PVDF) mixed slurry on the polyethylene terephthalate (PET) nonwoven in order to apply to lithium-ion batteries.

Diatomite has also found application in new generation batteries – supercapacitors or ionistors. For example, FeOOH nanosheets on porous diatomite have been successfully prepared by a facile two-step hydrothermal approach for supercapacitors [14]. The work [15] demonstrates a new and simple approach for fabrication a complex three-dimensional (3-D) composite for supercapacitor based on hollow diatom silica structures combined with interconnected coatings of TiO₂ nanospheres and MnO₂ mesoporous nanosheets (diatomite@TiO₂@MnO₂). The coating process is based on hydrolysis and metathetic reaction of TiF₄ precursor followed by the reaction with KMnO₄, which allows the coating of internal and external surface of diatom hollow structure with TiO₂ and MnO₂ layers. In [16] work, diatomite is used as the porous template for the in-situ growth of graphene layer, subsequently the CNTs arrays are uniformly grown on the graphene surface to form a hierarchical conductive framework.

Among the numerous modern composite materials, electrochemical materials are of great interest, which have highly complex properties and characteristics, particularly

anode composites of the carbon-nano dispersed silicon system [17-19]. Carbon and silicon anode matrices have attracted attention in recent years as anode materials, being a cheaper and more effective alternative to diamond matrices. Among carbon allotropes, the electrically conductive properties of CNTs were recognized after their official discovery in 1991, and they are regularly investigated as a filler in composites. Improving and/or tailoring the electrical conductivity of CNTs is not a novel idea, and multiple efforts to achieve higher performance have been reported, and most of them have focused on the doping of CNTs [20].

The purpose of the experiments described in this article was to obtain an anode from carbon nanotubes grown on the surface of diatomite. The utilization of this material as a substrate combines the advantage of both CNTs and diatomite, opening a promising potential application [21].

2. Materials and Methods

2.1 Synthesis.

Diatomite (sample 1) was treated with hydrochloric acid (HCl) (ratio of mineral to acid 1:14) at a temperature of 90°C for 2 h. Then the diatomite was washed into a neutral medium with distilled water. The medium's neutrality was measured by a universal indicator (pH~6-7). Then the samples were dried in a drying oven and cabinet, and the diatomite was calcined in a tube furnace at 500 °C.

Diatomite with carbon nanotubes (Diatomite/CNT) (sample 2). Carbon nanotubes were synthesized by chemical catalytic vapor deposition, described in [22]. The growth process was carried out by catalytic decomposition of a propane-butane gas mixture on a diatomite substrate with a pre-prepared catalyst. The method of producing carbon nanotubes includes impregnating diatomite with an alcohol solution of Ni(NO₃)₂*6H₂O, drying, and heating the reactor to a temperature of 800 °C in an inert media. The propane-butane gas mixture is then passed for 30 min at a rate of 90 cm³/min. The reactor is cooled to room temperature in argon for 1-1.5 h. Then remove the catalyst with carbon deposited on it. Thus, the catalyst particle adsorbs the initial carbon-containing compound and promotes the dissociation of this compound. The resultant carbon diffuses into the catalyst volume and, reaching saturation, forms nanotubes and nanofibers on the surface of the catalyst particle.

The obtained samples were examined by Scanning Electron Microscope analysis (SEM), Energy Dispersive X-ray analysis (EDAX), Brunauer-Emmett-Teller (BET) surface area analysis.

2.2 Battery assembling

Synthesized carbon materials were tested as anode in a half-cell battery with lithium foil. Diatomite (and CNT-diatomite), electroconductive component acetylene black and polyvinylidene fluoride (PVDF) in a weight ratio of 70:20:10 were blended with N-methyl-2-pyrrolidone (NMP). In case of other carbon materials (apricot stone, rice husks, walnut shell) a weight ratio was 80:10:10. Then the slurry was casted on the surface of the copper foil, dried in a vacuum oven for 4 h at a temperature of 60 °C. The prepared anode material was tested in a CR2032 (MTI®) type cell. The coin cell type batteries CR2032 were assembled in an argon filled glove box (Ar 99.999%, LABmaster Pro Glovebox, <0.1 ppm H₂O and O₂, MBraun, Germany). The electrolyte solution consisted of 1 M LiPF₆ in a mixture of ethylene carbonate, diethyl carbonate and dimethyl carbonate (EC/DEC/DMC, 1:1:1 v/v). Celgard 2400 polypropylene was used as a separator. Metallic lithium foil was used as both reference and counter electrodes.

2.3 Electrochemical tests

Electrochemical tests (galvanostatic charge-discharge cycling) were carried out in the range of potentials from 0.01 to 3.0 V and a rate of 50 mA/g on a multichannel tester (Neware Technology Ltd., China).

3. Results and Discussion

The results of the EDAX analysis of samples such as sample 1, sample 2 are shown in Fig.1. It can be seen from X-ray diffraction results that diatomite's contain metals, as, Ti, Si. For synthesis CNTs usually use hydrogen as a reducing agent, in this case, as a reducing agent served carbon that contains diatomite mineral. As shown by the results of an EDAX analysis of a diatomite sample after the synthesis of carbon nanotubes Fig. 1. (b) there is high carbon content, as well as metal particles as Ni it is because Ni(NO₃)₂·6H₂O used as catalyst. High carbon content can be attributed to the formation of carbon nanotubes during the decomposition of a propane-butane gas mixture on the surface of diatomite.

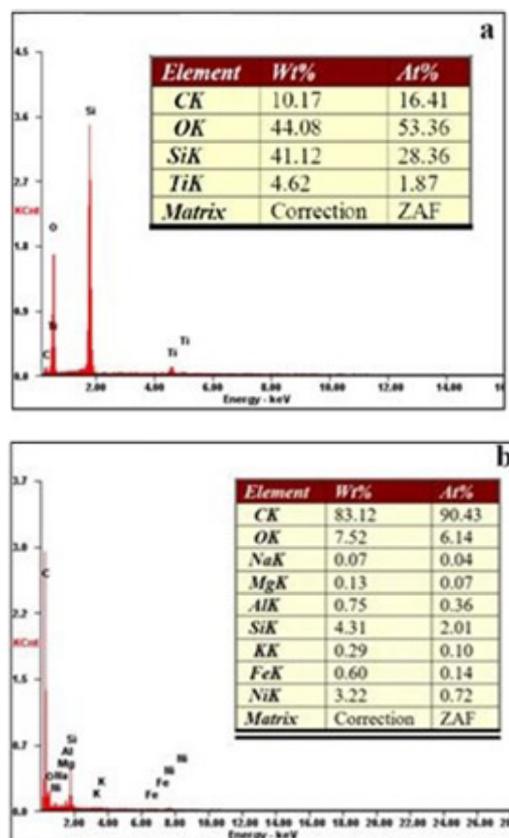


Fig. 1. EDAX analyses of samples: a – sample 1; b – sample 2.

Scanning electron microscopic images were obtained in accordance with elemental analysis, for the samples, as diatomite, CNT on the surface of diatomite (Fig. 2). Figure 2a shows a snapshot of the treated diatomite, where you can see the skeletons of diatoms and broken particles of diatoms. Diatomite has a micro- and nanoporous structure. Multi-walled carbon nanotubes obtained on the surface of diatomite presented in Fig. 2b. The diameter of carbon nanotubes were in the range of 78.4 to 81.8 nm.

A low specific surface area is characterized by treated diatomite and CNTs synthesized on the surface of diatomite, the reason for this is, most likely, the presence of a large amount of mineral components in the original precursor, which prevents the formation of a highly developed porous structure during the process of steam-gas activation. This fact indicates the need to apply the chemical activation method to this material with the subsequent leaching of the mineral part.

Table 1 represents the results of the BET analysis of samples.

The utilization of diatomite mineral as a substrate combines the advantage of both CNTs and diatomite. According to previous

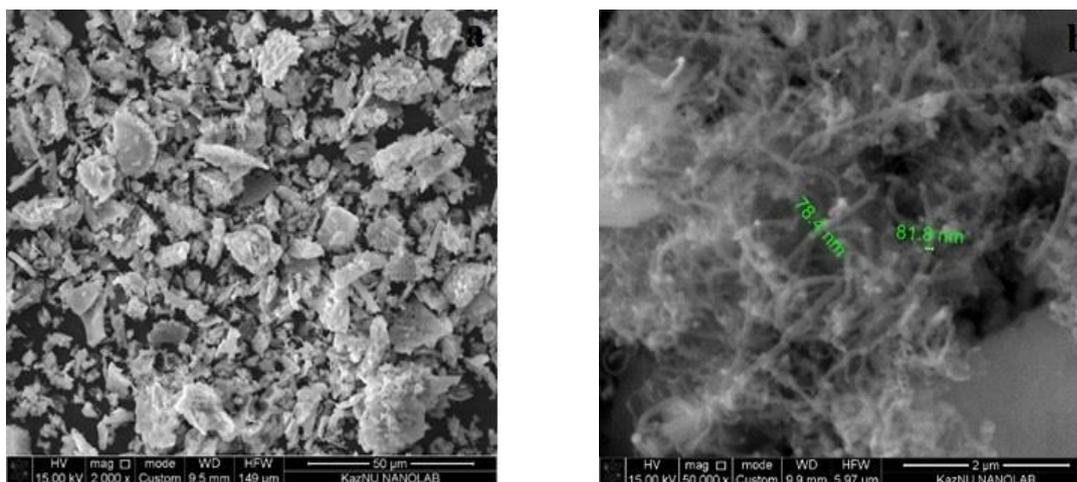


Fig. 2. SEM analyses of samples: a – sample 1; b – sample 2.

Table 1. The results of measurement of specific surface by the BET method

| № | Sample's name | Specific surface area, m^2/g | Specific capacity of battery, $\text{mA}\cdot\text{h}\cdot\text{g}^{-1}$ |
|---|---------------|--|--|
| 1 | Sample 1 | 39.1 | 100 |
| 2 | Sample 2 | 188.9 | 120 |

investigations [23], we suggest that obtained Sample 2 (Diatomite/CNT) is highly crystallized, retains the porous structure of diatomite and contains fewer impurities, therefore the specific surface area increased in comparison pure diatomite, Sample 1 (Table 1).

BET analysis shows that with an increase in the specific surface area of samples, the specific capacity of batteries increased.

The galvanostatic charge-discharge capacity of the 1st, 2nd, 10th cycles of the half-cells and cycling performance of electrodes with prepared electrodes are depicted in Fig. 3.

Due to the loose and porous structure of diatomite, as well as the porosity and enhanced surface area of composite materials based on diatomite and CNT, it allows the added material to mix with diatomite uniformly and increases the chance of reaction; and more bioactive phases are generated [24]. As reported in early papers, a chemical reaction between lithium ions and silica can lead to irreversible capacitance. The electrochemical reaction involves SiO_2 that is reduced to Si and the formation of amorphous Li_2O and crystalline Li_4SiO_4 . These reactions is considered as irreversible and corresponds to the formation of SEI layer and the reduction of SiO_2

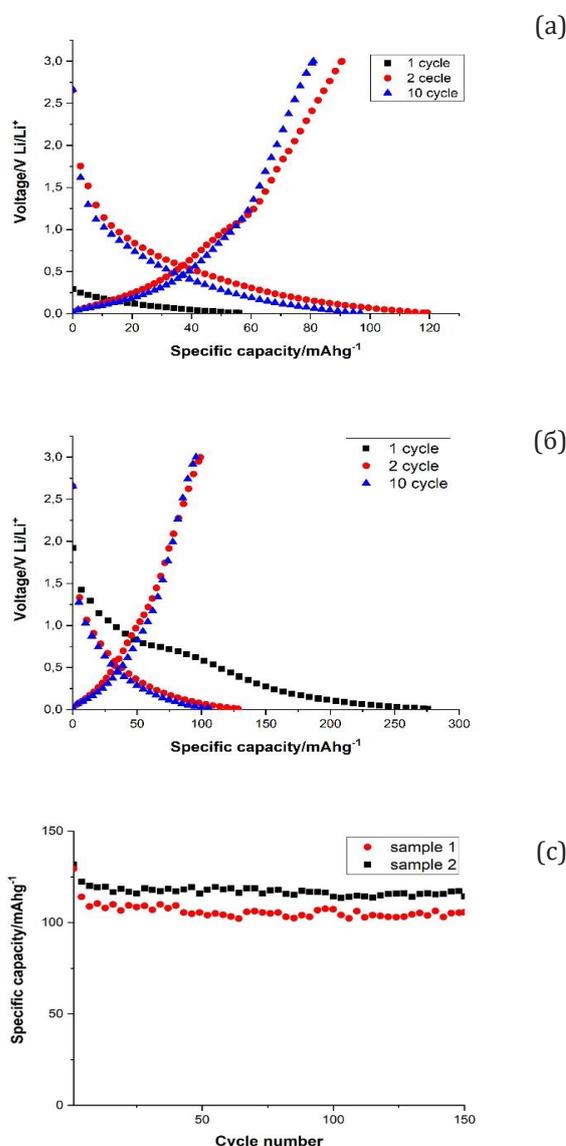


Fig. 3. Charge-discharge profiles of batteries with carbon electrodes: a – sample 1; b – sample 2; c – cycling performance of batteries with synthesized carbon electrodes.

[25]. The diatomite/CNT composite delivers a high discharge than pure diatomite of about 250 mA·h·g⁻¹. After 120 cycles, the discharge capacity is reduced to 150 mA·h·g⁻¹. Cells based on diatomite maintain a reversible capacity of 100 mA·h·g⁻¹.

4. Conclusions

Diatomite mineral (from Mugalzhar region) and carbon nanotubes grown on the surface of diatomite were used as electrodes for lithium-ion batteries. The obtained samples were examined by Energy Dispersive, X-ray analysis, Brunauer-Emmett-Teller analysis. The battery with sample 2 performed high performance of 120 mA·h·g⁻¹ over 150 cycles.

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Электродные материалы на основе диатоми-та для литий-ионных аккумуляторов

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Аннотация

Энергетика – чрезвычайно интересная область, которая стремительно развивается уже много лет подряд. Сегодня публикуются самые разные статьи об альтернативных источниках энергии, аккумуляторах и суперконденсаторах. Эта статья о литий-ионном аккумуляторе. Аккумуляторы состоят из трех отдельных частей, одна из которых является анодом. Именно в этой области скапливаются электроны, обеспечивающие питание электрических устройств. С 2011 года в литиевых батареях чаще всего используются графитовые аноды. Обладая потенциалом удерживать во много раз больше энергии, чем графит, кремний является заманчивым предложением для ученых, работающих над литиевыми батареями следующего поколения. Кремний является перспективным материалом для анодов литий-ионных аккумуляторов нового поколения, так как в процессе электрохимического введения способен накапливать большое количество лития (до 4,4 атома Li на атом Si) и обеспечивать очень высокие значения удельной емкости (4200 мАч/г). В настоящей статье рассмотрены перспективы использования кизельгура (ДЭ) (Мугалжарского района) в секторе непрерывного развития энергетической науки и техники. Экологически чистый диоксид кремния и производства кремния, кизельгур имеет необходимую нано-микроструктуру, которая предлагает преимущества, присущие существующим и новым приложениям в электрохимии, катализе, оптоэлектронике и биомедицинской инженерии. Было обнаружено, что кремний, и материалы на основе кремния полезны для хранения и накопления энергии. Также для сравнения поверхность ДЭ была модифицирована нанотрубками. Электродный материал был охарактеризован методами EDAX, SEM, BET и электрохимическими методами. Полученные результаты показали преимущество модифицированного диатомита

(удельная поверхность – 188,9 м²/г и удельная емкость аккумулятора – 120 мАч/г) по сравнению с немодифицированным (удельная поверхность – 39,1 м²/г и удельная емкость аккумулятора) – 100 мАч/г).

Ключевые слова: диатомит, УНТ, электрохимический электрод, аккумуляторы.

Диатомит негізіндегі литий-ионды аккумуляторларға арналған электродтық материалдар

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Аннотация

Энергетика – бұл көптеген жылдар бойы қарқынды дамып келе жатқан өте қызықты сала. Бүгінгі таңда баламалы энергия көздері, батареялар және суперконденсаторлар туралы әртүрлі мақалалар жарияланады. Бұл мақала литий-иондық батарея туралы. Батареялар үш бөлек бөліктен тұрады, олардың бірі анод. Дәл осы аймақта электрондар жиналып, электр құрылғыларына қуат береді. 2011 жылдан бастап графит анодтары литий батареяларында жиі қолданылады. Графитке қарағанда бірнеше есе көп энергияны сақтайтын әлеуеті бар кремний литий батареяларының келесі буынында жұмыс істейтін ғалымдар үшін қызықты ұсыныс болып табылады. Кремний жаңа буынның литий-иондық аккумуляторларының анодтары үшін перспективалы материал болып табылады, өйткені электрохимиялық енгізу кезінде ол литийдің көп мөлшерін (Si атомына 4,4 Li атомына дейін) жинақтай алады және өте жоғары мәндерді қамтамасыз етеді. меншікті сыйымдылығы (4200 мАч/г). Бұл мақалада энергетикалық ғылым мен техниканың үздіксіз дамуы секторында диатомды жерді (ДҚ) (Мұғалжар ауданы) пайдалану перспективалары қарастырылады. Экологиялық таза кремний және кремний өндірісі, кизельгур электрохимия, катализ, оптоэлектроника және биомедициналық инженериядағы бар және жаңа қолданбаларға тән артықшылықтарды ұсынатын маңызды нано-микроқұрылымға ие. Крем-

ний, кремний және кремний негізіндегі материалдар энергияны сақтау және сақтау үшін пайдалы екені анықталды. Сондай-ақ, салыстыру үшін DE беті нанотүтікшелермен модификацияланды. Электродтық материал EDAX, SEM, BET және электрохимиялық әдістермен сипатталды. Алынған нәтижелер модификацияланған диатомиттің (спецификалық беті

– 188,9 м²/г және аккумулятордың меншікті сыйымдылығы – 120 мАч/г) модификацияланбағанмен салыстырғанда (меншікті беті - 39,1 м²/г және аккумулятордың меншікті сыйымдылығы) артықшылығын көрсетті – 100 мАч/г).

Клт сөздер: диатомит, КНТ, электрохимиялық электрод, батареялар.