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Silica from Kazakhstan Rice Husk as an Anode Material for LIBs

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Abstract

This paper reports the synthesis of the silica (SiO_2) from Kyzylorda rice husk (RH) and investigation of its electrochemical behaviour as an anode material for the lithium-ion battery. Rice husk, considered as agricultural waste material, contains a substantial amount of amorphous silica, carbon, and minor other mineral composition, which have potential industrial and scientific applications. Due to the high theoretical capacity of silicon (4200 mAh g^{-1}) and silicon dioxide (1965 mAh g^{-1}), Si-containing compounds are considered as a promising candidate for a new generation of anode materials for lithium-ion batteries. In this work, the technology of amorphous SiO_2 extraction from Kyzylorda region rice husk is developed. The silica powder was obtained by burning the rice husk and treating the obtained ash with the sodium hydroxide and hydrochloric acid. The extracted SiO_2 and intermediate products were studied by the SEM, XRD, XRF, XPS, TGA in comparison with commercial silica. The RH of the Kyzylorda region has 12% of Si. The electrochemical characteristics of assembled coin cell type battery were tested by using cyclic voltammetry and galvanostatic charge/discharge cycling. Results show that silica synthesized from agriculture waste has the same performance as commercial analog. The initial discharge capacity of the battery with synthesized silicon dioxide was 1049 $mAhg^{-1}$. The reversible discharge capacity in the second and subsequent cycles is about 438 $mAhg^{-1}$.

1. Introduction

The production of rice forms a large amount of agricultural waste as straw, husk, and flour. Straw is usually burned in the fields, because the cost of its collection is 2–3 times more expensive than rice, despite that it causes damage to the fertile layer of earth and the atmosphere. Due to the large content of silica, the rice husk (RH) does not burn with an open flame and does not decompose completely, also it is not used as a food for animals. Annually about 600 million tons (MT) of rice is produced (20% or 120 MT is RH), which consists 12% of silica (or 14.4 MT) [1–2]. RH waste is being considered as a sustainable and renewable resource and has high potential as a low-cost precursor for the production of value-added materials. Besides, RH is used in power plants as fuel, as fillers, packaging material, insulators, abrasives, building materials [3–14]. The more valuable application of RH and rice husk ash (RHA) in the industry is desired.

Silica and silicon-containing compounds (SiOx) are considered as a promising candidate for a new generation of anode materials for rechargeable lithium-ion batteries (LIBs). These materials have a very high theoretical capacity: silicon (4200 mAh g^{-1}), silicon dioxide (1965 mAh g^{-1}), which exceeds by several times the capacity of the conventional anode as graphite [15–16]. Several works have been published on silicon and silicon oxide, obtained from RH and used as an anode material of LIBs [17–23]. The RH composition depends on the plant variety and soil composition of the field. In addition, the rice husk ash is sensitive to the methods of combustion (with and without air), which effects on the content of extracted compounds. Structure of the formed silica also based on combustion temperature:

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amorphous SiO_2 is formed at 550–750 °C, crystalline SiO_2 is at 800–1000 °C. But the synthesis of silica from sand requires the use of high temperatures (up to 2 000 °C) [24–25].

Shen Y. [19] reviewed the published methods for the RH silica-delivered nanomaterials for the battery application. The recent progress of methods for producing different structural SiO_2 and Si from RH and its electrochemical properties when used as an anode material in the LIBs have been checked.

Cui J. et al. [21] prepared micro-sized porous C/SiO_2 composites from rice husks through a facile carbonization process using $ZnCl_2$ as activating agent under argon atmosphere. This porous C/SiO_2 composite exhibits high discharge specific capacity (1105 mAhg^{-1} at 0.1 A/g), excellent cycling stability and good rate capability.

Kazakhstan consumes and grows a large amount of rice – more than 65% from other types of cereals. 161.4 thousand hectares were planted in Kyzylorda region in 2016, and 81.2 thousand hectares were used for rice. However, there is no complete production cycle for processing and obtaining additional types of industrial products in Kazakhstan rice industry. Agricultural waste is a multi-tonnage and renewable raw material, the rational use of which contributes to the preservation of ecological balance in nature. The process of obtaining silicon dioxide from RH consists of simple methods of treating with chemicals and burning at medium temperatures (less than 1000 °C). Therefore, the aim of this research is to develop the technology of extraction amorphous silica from local Kyzylorda region RH and to test it as an anode material for LIBs.

2. Experimental

The main stages of synthesizing the silica from rice industry waste are the washing of RH, obtaining the RHA, producing the silicon dioxide. The setup diagram for the synthesis of SiO_2 is presented in Fig. 1.

2.1. Preparation of RHA

The RHs from the Kyzylorda region were rinsed with water at room temperature to remove mechanical contaminants and dust and then dried at 100 °C. The washed and dried RH was treated with aqueous HCl solution (10%) for 2 h to hydrolyze the cellulose and hemicellulose and dissolve the metal impurities. Then it was rinsed by water until reaching the pH = 7 and dried at 100 °C. After that the RH was burnt in a muffle furnace in two stages: first at 500 °C for 2 h, then at 700 °C for 2 h [26].

2.2. Production of silicon oxide

The RHA was dissolved in 2M NaOH (NaOH: RHA = 2: 1) at 90 °C for 2 h. The resulting muddy solution was filtered. Then, hydrochloric acid was added to obtain silica gel, which is formed at pH = 7. The silica gel was rinsed by water to remove impurities and dried in a drying oven at 110 °C.

2.3. Characterization

The microstructure of samples was observed by scanning electron microscope (SEM) (JEOL JSM-7500F). Thermal gravimetric analysis (TGA) was performed with TA instruments (Q500 V20.13) in an air atmosphere. X-ray powder diffraction patterns (XRD) were done using Ultima IV Rigaku. Elemental composition of samples was determined by X-ray fluorescence (XRF) Axios Max PANalytical. The X-ray photoelectron spectra (XPS) were obtained on a spectrometer Sigma Probe (Thermo VG Scientific). The energy 1.0 eV was used to record the survey spectrum and energy 0.05 eV for the recording of separate spectra. Elemental analysis of synthesized silica was carried out using energy dispersive X-ray spectroscopy (EDS).

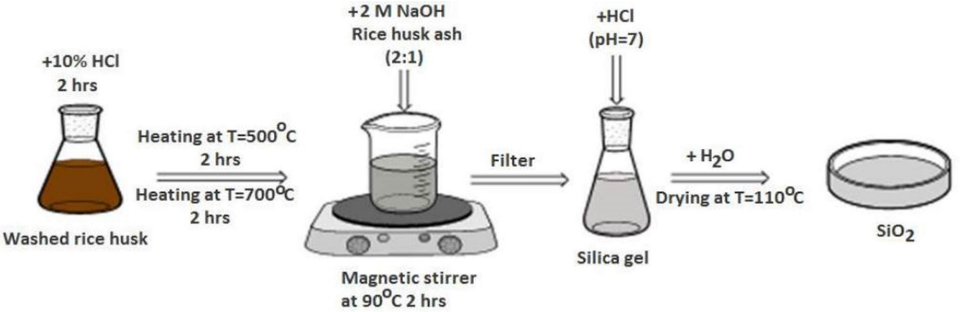


Fig. 1. The setup diagram for the synthesis of SiO_2 from RH.

2.4. Battery assembling and testing

Synthesized silica, carbon and carboxymethylcellulose (CMC) in a ratio 40:40:20 were blended with water until the homogeneous slurry was prepared. Then the slurry was cast on the surface of the copper foil, dried in a vacuum oven for 4 h at a temperature of 100 °C. The coin cell type batteries CR2032 were assembled in an argon-filled glovebox (MBraun, Germany). The electrolyte solution consists of 1 M $LiPF_6$ 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. The general scheme of the half-cell battery is SiO_2/KB/CMC|$LiPF_6$ (1M)|Li. For comparison purpose, electrodes with the commercially available SiO_2 powder were fabricated (637238 Aldrich) in the same way and tested.

Cyclic voltammetry (CV) and galvanostatic charge/discharge cycling of the assembled batteries were conducted at ambient temperature using BioLogic Science Instruments (France), Neware Technology Ltd. (China). The scan rate for CV was 0.1 mV/s with a voltage range of 0.01–3.0 V.

3. Results and discussion

The morphology of RH surface before and after washing with water was observed by SEM (Fig. 2a, b). It can be seen from the pictures that impurities are present on the surface of the initial RHs (Fig. 1a), whereas after washing it has become pure (Fig. 1b).

Figure 2c shows a curve of RH weight loss during heating in an air atmosphere up to 800 °C. It can be seen, that the initial loss of RH mass starts at 100–150 °C, which is caused by the evaporation of water and highly volatile substances. In the second stage, there is a rapid decrease in weight in the temperature range of 250–350 °C, which, according to the literature [27], corresponds to the decomposition of the least stable hemicellulose and cellulose. In the temperature range 350–550 °C, more stable aromatics decompose. The weight of the RH sample stabilized in the temperature range 550–600 °C. It can be assumed that the RHs from the Kyzylorda region contains up to 87.9% of organic volatile components and up to 12.1% of inorganic ones (silicon and metal impurities).

From Fig. 3a, it can be seen that the morphology of RH after burning has been changed. The surface of RHA is tuberculate as RH’s one, but it destructed during the burning and twisted in the tube form. XRD analysis of RHA (Fig. 1b) revealed the peaks of crystallized composites, such as calcium silicate ($CaSiO_4$), dicalcium silicide (Ca_2Si), magnesium silicide (Mg_2Si), silicium, magnesium oxide, phosphorus.

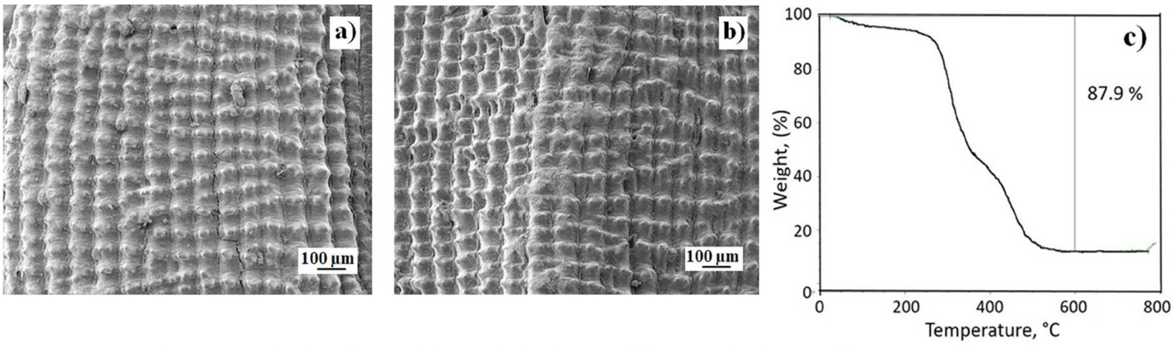


Fig. 2. Analysis of RH: (a) – original RH; (b) – washed RH; (c) – TGA curve.

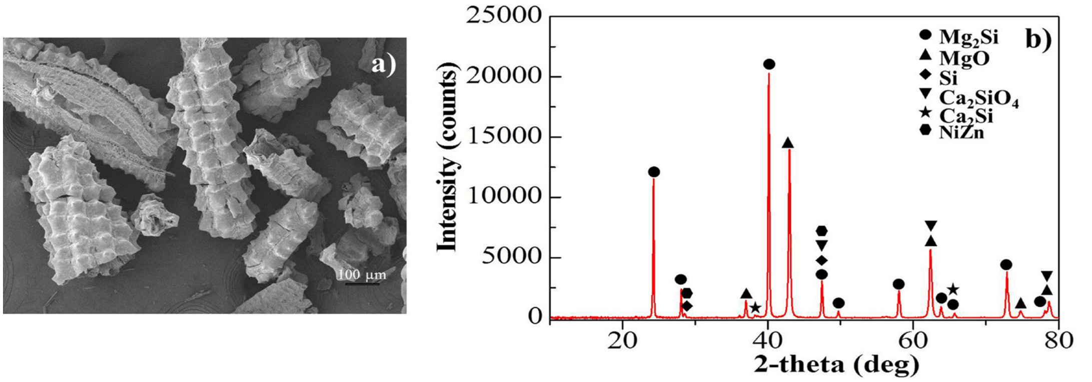


Fig. 3. RH ash analysis: (a) – SEM image; (b) – XRD.

Table
The composition of RH, RHA before and after treatment with HCl

Element	RH	RHA	RHA after leaching with HCl
O	10.443	9.220	11.846
Mg	0.172	0.199	0.047
Al	0.140	0.123	0.228
Si	62.584	59.120	80.741
P	2.201	1.703	2.411
S	0.607	0.729	-
Cl	0.714	1.213	-
K	11.215	17.690	1.538
C	9.957	8.249	1.871
Mn	0.654	0.645	0.116
Ti	0.125	-	0.125
Fe	0.648	0.797	0.681
Ni	0.062	0.052	0.062
Zn	0.564	0.161	0.044
Sr	0.065	0.099	-
Cu	0.036	-	-

Table presents a comparative data on the elemental composition of RH, RHA before and after treatment with hydrochloric acid. Original RH consists of 62% of silicium. The average content of potassium, oxygen, calcium is about 10%, phosphorus is about 2%. The amount of such elements, like chlorine, magnesium, iron, sulfur, zinc, manganese, aluminium, titanium, strontium, nickel and copper is extremely small (less than 1%), and even the total amount of them is only 3.6%.

Acid treatment of RHA showed efficiency in removing of impurities. Thus, sulfur, chlorine, and strontium were completely removed and content of such elements as magnesium, potassium, calcium, manganese, iron, and zinc decreased. Si-content has increased up to 80%.

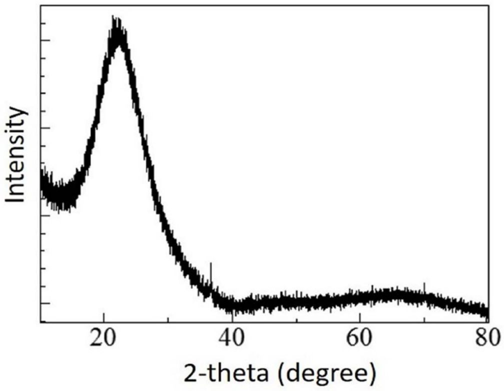


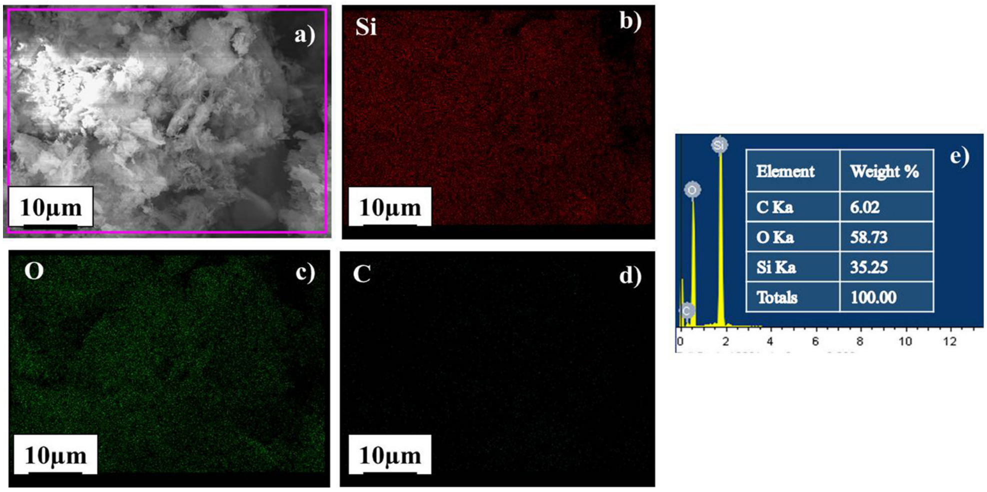
Fig. 4. X-ray curves of amorphous silicon oxide.

The process of silica synthesis from RH can be represented by the equations [28]:

$$SiO_2 + 2Na(OH) \rightarrow Na_2SiO_3 + H_2O$$
$$Na_2SiO_3 + 2HCl \rightarrow H_2SiO_3 + 2NaCl$$
$$H_2SiO_3 \rightarrow SiO_2 + H_2O$$

The XRD analysis of synthesized silicon oxide (Fig. 4) showed the formation of a single wide peak at approximately 2θ = 22 ° can be assigned to the disordered amorphous structure of silica [2].

As shown in Fig. 5, silicon and oxygen are distributed very uniformly and the synthesized SiO_2 consists mainly of SiO_2. Sample contains around 6 wt.% of carbon as well (Fig. 5e), which is hardly noticeable from the Fig. 5d, due to the scale and small amount. Presumably, carbon could form from the residues of organic components in the initial RH.



Element	Weight %
C Ka	6.02
O Ka	58.73
Si Ka	35.25
Totals	100.00

Fig. 5. SEM-EDS analysis of SiO_2 from RHA: (a) – SEM image, compositional maps for (b) – Si; (c) – O; (d) – C and (e) – electron dispersion spectrum.

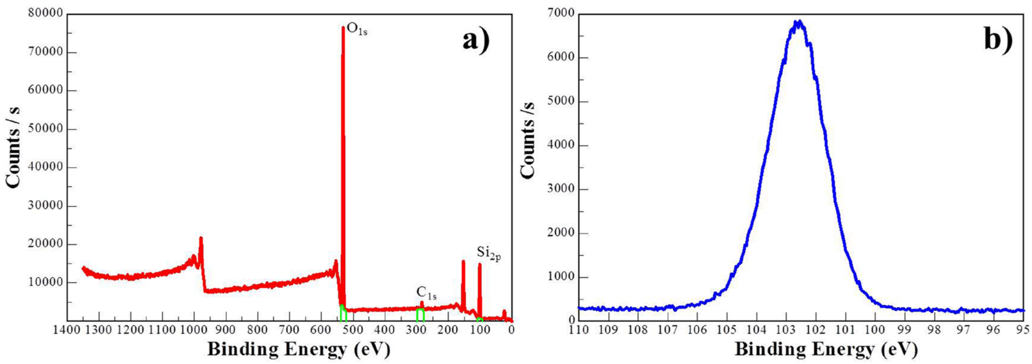


Fig. 6. XPS spectrum of the synthesized SiO_2: a – XPS survey spectrum, b – Si 2p scan.

Synthesized silicon dioxide was analyzed using XPS to study the elemental composition, chemical and electronic states of atoms (Fig. 6).

Figure 6a shows an overview XPS spectrum of SiO_2 synthesized from RHs in which spectra of silicon, oxygen, and carbon are visible (Fig. 6a). The XPS spectra have a line attributed to Si with a binding energy around 102.8 eV, which is characteristic to SiO_2 (Fig. 6b).

In order to evaluate the feasibility of synthesized amorphous silica as the anode material for LIBs the electrochemical tests were carried out. The cells were assembled with Li metal and synthesized amorphous silica, then investigated by cyclic voltammetry and galvanostatic charge/discharge cycling in the range of potential from 0.01 to 3.0 V and current density 50 mA g^{-1}.

The assembled battery with SiO_2 from RH (Fig. 7c, d) showed that the electrochemical properties are not inferior to commercial analogs (Fig. 7a, b).

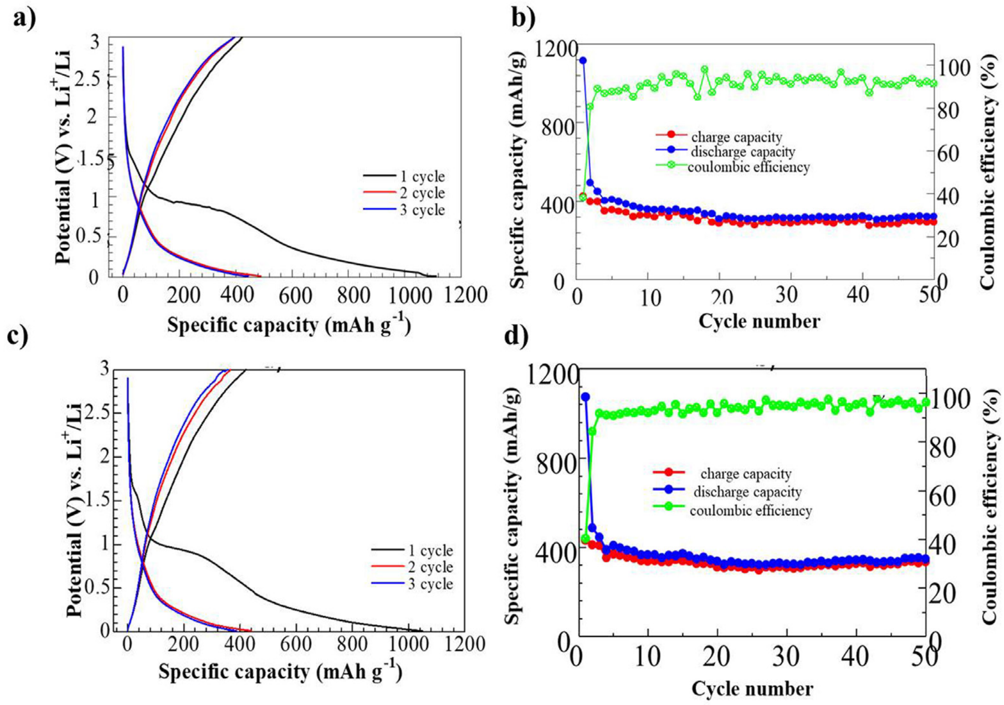


Fig. 7. Comparison of electrochemical parameters of silicon oxide: (a), (b) – commercial silicon dioxide; (c), (d) – silicon dioxide synthesized from RH.

The initial discharge capacity of the battery with commercial silica was 1035 $mAhg^{-1}$ and 1049 $mAhg^{-1}$ with synthesized silicon dioxide. Both batteries have a plateau at 1 V on the discharge curve of the first cycle due to the formation of a solid electrolyte interface (SEI) and byproducts. The reversible discharge capacity in the second and subsequent cycles is about 438 $mAhg^{-1}$. The capacity after the 50 cycles is 89%, while the coulombic efficiency is as high as 97%.

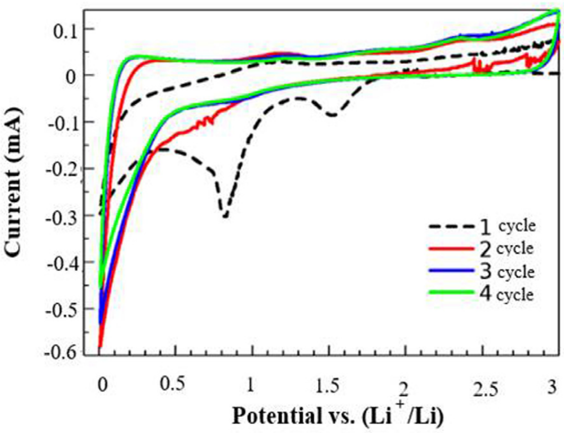


Fig. 8. CV plots of a battery with a synthesized SiO_2 from RH.

Figure 8 shows a cyclic voltammogram of an electrochemical system with synthesized SiO_2 in the voltage range from 0.01 and to 3 V at a scan rate of 0.1 mVs^{-1}. Wide cathode peaks in the region of 0.8 V and 1.5 V, which appear only in the first cycle, indicate the decomposition of the electrolyte and the formation of a solid electrolyte protective film, which correlates with charge-discharge behavior shown in the Fig. 7. There is an irreversible electrochemical reaction between lithium ions and silicon dioxide with the formation of an inert phase of Li_2O or Li_4SiO_4 [29–31]. This results in a significant loss of capacity during the first cycle. The peaks of the cyclic voltammogram coincide with the two plates on the galvanostatic discharge/charge curve of the first cycle (Fig. 7a, b).

Thus, it can be concluded based on an electrochemical study of LIB with SiO_2 synthesized from RH, that it exhibits the same properties as commercial SiO_2. Electrochemical data correspond to published literature data.

4. Conclusions

In summary, the silica from RH of the Kyzylorda region has been successfully extracted and electrochemically tested as a potential anode material for LIBs. The comparison of electrochemical properties of SiO_2 from RH with commercial silica showed similar properties. Electrochemical data correlates with published works on silica extracted from RH of other origins. The discharge capacity (delithiation) reached 1049 $mAhg^{-1}$ in the first cycle, in the second it showed 438 $mAhg^{-1}$ at 0.01 and 3.0 V. This drastic capacity fading during the first cycles occurs due to formation of SEI layer and irreversible products of silicate/LiO_2, which are common for SiO_2 anode. The capacity, starting from second cycle, shows good stability without additional modification of silica. Characterization of the product synthesized from RH was carried out using TGA, SEM, XPS, EDS methods. Amorphous structure of synthesized silicon dioxide was proven. The RH of the Kyzylorda region has 12% of Si. The technology of obtaining amorphous SiO_2 from RH in laboratory scale has been worked out. In the future, this cheap technology might be commercialized, since Kazakhstan has huge resources for processing of RH waste. It is shown that valuable products as amorphous silica can be obtained from a plant waste by the simple and cost-effective way.

Acknowledgments

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