Electrochemical and electron microscopic characterisation of solid-disk shungite electrodes

(Elektrochemická a elektronově mikroskopická charakterizace pevných diskových šungitových elektrod)

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Abstract

Two different types of shungites were tested as promising electrode material for electroanalysis. Noble elite and black raw shungite stones were subjected to microscopic and elemental analysis using scanning electron microscopy and energy-dispersive X-ray spectroscopy, respectively. These stones were mechanically shaped into cylinders and then embedded into plastic tubes equipped with an electrical contact, giving rise to the appropriate solid-disk electrodes. Cyclic voltammetric measurements with pure 0.1 mol L^{-1} Britton-Robinson buffer (pH 7) and 1 mmol L^{-1} potassium ferrocyanide at scan rate ranging from 20 to 300 mV s^{-1} were carried out to determine the corresponding double-layer capacitances, heterogeneous electron transfer rate constants, charge transfer coefficients, exchange-current densities, and electrochemically active surface areas. Compared to a commercially available glassy carbon electrode, only electrode derived from carbon-rich elite shungite (90.6–94.1%) could eventually serve as several times cheaper alternative.

Key words: Shungite, Scanning electron microscopy, Energy-dispersive X-ray spectroscopy, Electrochemical kinetics, $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ redox couple.

Introduction

In general, shungite is defined as a unique Precambrian carbonaceous natural mineral of organic origin that can be found in its raw form only in the Republic of Karelia, the Russian Federation. This mineral received its name from a small village called Shunga where it was first discovered. Shungite stones are classified into five categories according to carbon content. However, a trivial division took hold in the lay public, namely to noble elite shungite with a silvery surface (≥90 % carbon; type I), gray Petrovsky shungite (50-70 % carbon; type II), and black regular shungite (30-50 % carbon; type III). The shungite represents a rather amorphous carbon in sp2 and sp3 types, with well-developed mono- or stacked graphene layers (≤200 nm) which form spatially arranged, curved, and bent fractals [1]. Besides, shungite contains (<0.001% *w/w*) multi layered fullerene-like globules with a diameter of 10-30 nm. However, numerous impurities (mineral veins) of quartz (SiO_2), aluminosilicates ($NaAlSi_3O_8$), feldspars, carbonates, mica, pyrite, and metal (Al, Mg, Ti, and Na) oxides can be visible to the naked eye in less noble shungites [2]. In this study, raw stones of regular and elite shungite were machined into cylindrical shapes to form the corresponding solid-disk elite shungite (EShE) and regular shungite (RShE) electrodes. The resulting shungite-based sensors with relatively low electrical resistivity (≥10 Ω cm) [3] were compared with the standard glassy carbon electrode (GCE) in electrochemical behaviour of ferro/ferricyanide redox couple. In addition, shungite stones were also subjected to microscopic and elemental analysis, whereas the obtained results were reflected with those from electrochemical kinetics studies.

Experimental part

Potassium hexacyanoferrate(II) trihydrate (≥99.95% trace metals basis) was purchased from

Merck KGaA (Darmstadt, Germany). Sodium hydroxide, 98.5% boric acid, 85% phosphoric acid, and glacial acetic acid were from Lach-Ner s.r.o. (Neratovice, Czech Republic). A deionized water with resistivity of 18.3 MΩ cm obtained from Milli-Q® deionization unit from Merck Millipore (Burlington, USA) was used for preparation of 0.01 mol L^{-1} $K_4[Fe(CN)_6]$ stock solution and 0.1 mol L^{-1} Britton–Robinson buffers (BRB) of different pH values.

Raw stones of elite and regular shungite were mechanically shaped into rollers (height 10 mm and diameter 8 mm) using EcoMet 30 manual grinding and polishing machine from Hanyko Praha s.r.o. (Praha, Czech Republic), whereas self-stick sanding papers WS flex 18 C with silicon carbide of different grit levels (60–320) from Hermes Schleifmittel GmbH (Hamburg, Deutschland) were chosen. The obtained rollers were embedded into cavity of plastic pipes with metal springs which served as electrical contact, as shown in Fig. 1.

Fig. 1. Image of home-made solid-disk elite shungite electrode.

Scanning electron microscopy (SEM) with the backscattered-electron (BSE) and secondary-electron (SE) modes for imaging raw shungite stones microstructures and energy-dispersive X ray spectroscopy (EDX) for elemental analysis were performed by TESCAN VEGA3 SBU with EDX probe Bruker X-Flash Detector 410-M from TESCAN s.r.o. (Brno, Czech Republic).

Each electrochemical experiment was carried out in a glass voltammetric cell containing 10 mL of 0.1 mol L^{-1} BRB with immersed GCE, EShE or RShE, followed by a silver chloride refence electrode with 3 mol L^{-1} KCl salt bridge from Metrohm (Herisau, Switzerland) and a platinum sheet from Elektrochemické detektory (Turnov, Czech Republic), acting as counter electrode. The chosen variant of electrode setup was connected to a potentiostat/galvanostat Autolab (model PGSTAT101) operated through NOVA 1.11 software, both from Metrohm.

To compare values of double-layer capacitance (C_{DL}), cyclic voltammetry (CV) measurements of pure 0.1 mol L^{-1} BRB (pH 7) were carried out at potential step (E_{step}) of 5 mV and scan rate (v) ranging from 0.05 to 1.50 V s^{-1}. To determine the electrochemically active surface areas (*ECSA*), heterogeneous electron-transfer rate constants (k_0), exchange-current densities (j_0), and charge-transfer coefficients (α), similar electrochemical experiments with 1 mmol L^{-1} potassium ferrocyanide in the same buffer at potential step of 5 mV and scan rate ranging from 0.02 to 0.3 V s^{-1} were performed.

Results and discussion

Microscopic and elemental analysis of elite and regular shungite stone helped to find out significant difference in their chemical compositions. Elite shungite (90.6-94.1 % C) resembled a smooth homogeneous carbonaceous material, very similar to glassy carbon.

Unlike the previous case, the regular black shungite (62.3–64.2 % C) can be defined as a fragmented (rough surface) material with an admixture of many impurities (minerals) which form druses (pyrite and aluminosilicates) and veins (quartz) [3], as seen in Fig. 2. According to this finding, the elite shungite should be preferred over regular shungite for the fabrication of solid disk electrodes applicable in the electroanalysis.

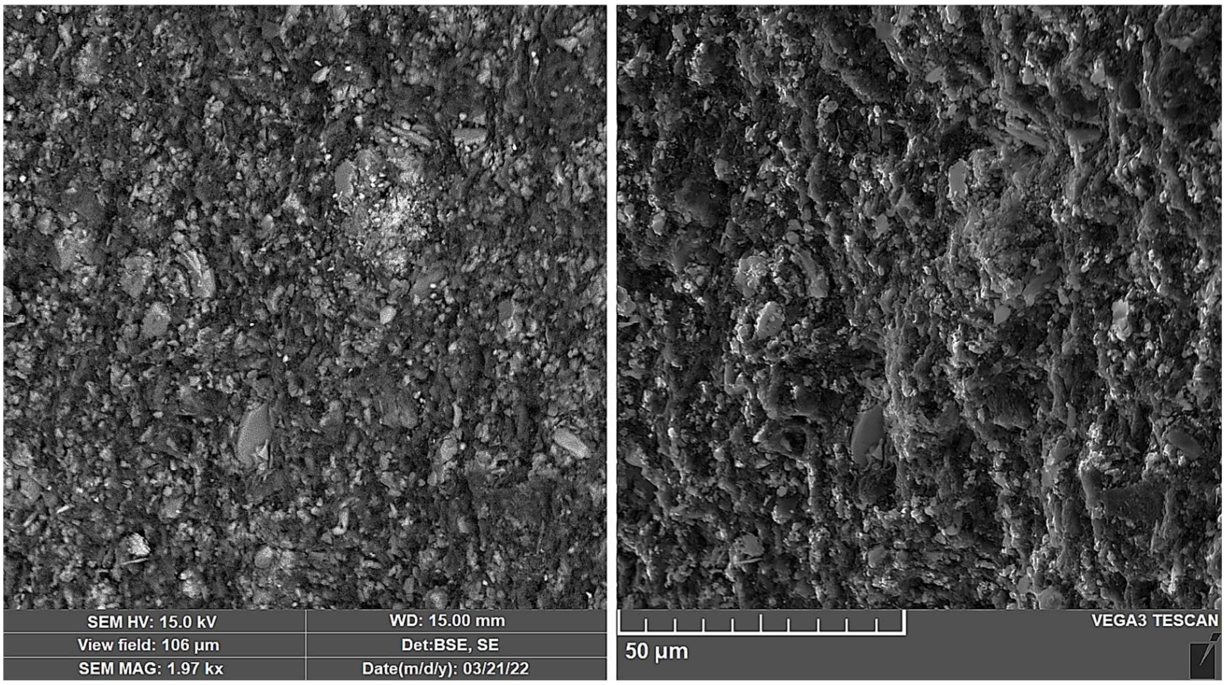

Fig. 2. Typical SEM images (~1.97×10^3 magnification) of a regular shungite stone.

Comparing to GCE, shungite-based electrodes can be characterised with a similarly broad cathodic and slightly shorter anodic range. A significant increase in double-layer capacitance in the case of the RShE (192.0 $\mu F\ cm^{-2}$) in comparison with GCE (27.6 $\mu F\ cm^{-2}$) and EShE (45.7 $\mu F\ cm^{-2}$) was probably caused by the low content of carbon and high proportion of impurities (SiO_2 and FeS_2). If their values of electrochemically active surfaces and geometrical surfaces are divided ($ECSA/A_{geo}$), it will be found that $ECSA$ decreases in this order EShE > GCE > RShE [3].

The linear relationships of log current density (j) on overpotential (η), known also as Tafel behaviours, were extrapolated ($R^2 > 0.9924$) to yield the values of the exchange-current densities (j_0) and barrier-symmetry factor (β), which could be replaced by the charge-transfer coefficients (α) for the investigated single-step reaction (Fe^{3+} to Fe^{2+}). As the j_0 value reflects the spontaneous reaction rate at equilibrium potential, it can be deduced that elite shungite (4.3×10^{-6} A cm^{-2}) is preferable to regular black shungite (8.7×10^{-7} A cm^{-2}). From the corresponding Tafel plots, the calculated α values for the EShE and GCE were close to a theoretical value of 0.5, indicating the symmetry of the energy barrier. This fact was also confirmed by the calculated $|i_p^a/i_p^c|$ values that varied from 1.018 to 0.976 for the EShE and from 0.986 to 1.090 for the GCE [3].

A Nicholson method [4] based on kinetic parameter Ψ (dimensionless quantity) was used for determination of heterogeneous electron-transfer rate constants (k_0), as demonstrated for GCE in Fig. 3. The rate of electron-transfer was determined two times higher for RShE (0.0159 $cm\ s^{-1}$) than for GCE (0.0069 $cm\ s^{-1}$) and EShE (0.0078 $cm\ s^{-1}$). A logical explanation can be seen in the presence of the above-mentioned conductive impurities

(≥20.4 % Fe), which probably significantly compensate a lower amount of carbon, as also evident from comparable *ECSA* values[3].

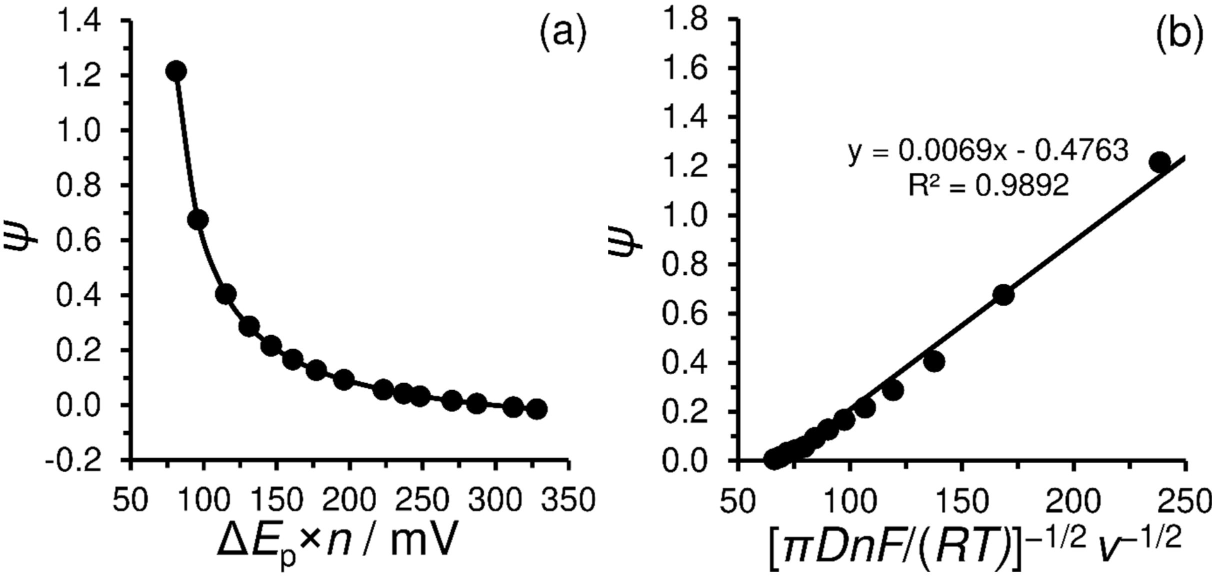

Fig. 3. Plot of ψ values vs. $\Delta E_\mathrm{p} \times n$ for kinetics of ferro/ferricyanide redox couple at GCE with diammeter of 3 mm (a). Plot of ψ vs. $[\pi DnF/(RT)]^{-1/2}$ $\nu^{-1/2}$ for the oxidation of 1 mmol L^{-1} potassium ferrocyanide in 0.1 mol L^{-1} BRB (pH 7) where the used diffusion coefficient (*D*) equal to 7.2×10^6 cm^2 s for ferricyanide in aqueous environment at 25 °C was obtained from the literature[5]. The values of ψ were calculated from the experimental ΔE_p values.

Conclusions

From all above-mentioned facts, it can be concluded that solid-disk electrodes manufactured from elite shungite stones represent a promising electrode material exhibiting similar electrochemical properties as many times expensive glassy carbon. On other hand, a limited utilization of regular shungite in electroanalytical applications can be assumed due to presence of numerous electroactive impurities.

Acknowledgements

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References

1. Kovalevski V.V., Buseck P.R., Cowley J.M.: Comparison of carbon in shungite rocks to other natural carbons: An X-ray and TEM study. Carbon *39*, 243 (2001).
2. Chou N.H., Pierce N., Lei Y., Perea-López N., Fujisawa K., Subramanian S., Robinson J.A., Chen G., Omichi K., Rozhkov S.S., Rozhkova N.N., Terrones M., Harutyunyan A.R.: Carbon-rich shungite as a natural resource for efficient Li-ion battery electrodes. Carbon *130*, 105 (2018).
3. Sýs M., Bártová M., Bartoš M., Švancara I.; Mikysek T.: Shungite (mineralized carbon) as a promising electrode material for electroanalysis. Materials *16*, 1217 (2023).
4. Nicholson R.S.: Theory and application of cyclic voltammetry for measurement of electrode reaction kinetics. Anal. Chem. *37*, 1351 (1965).
5. Moldenhauer J., Meier M., Paul D.W.: Rapid and direct determination of diffusion coefficients using microelectrode arrays. J. Electrochem. Soc. *163*, H672 (2016).