Active Carbon Modified by Rhenium Species as a Perspective Supercapacitor Electrode

Mateusz Ciszewski 1,* , Andrzej Koszorek 2, Łukasz Hawełek 3, Małgorzata Osadnik 4, Katarzyna Szleper 5 and Michał Drzazga 1

1 Hydrometallurgy Department, Łukasiewicz Research Network—Institute of Non-Ferrous Metals, Sowińskiego 5, 44-100 Gliwice, Poland; michald@imn.gliwice.pl
2 Department of Inorganic Chemistry, Analytical Chemistry and Electrochemistry, Silesian University of Technology, B. Krzywoustego 6, 44-100 Gliwice, Poland; Andrzej.Koszorek@gmail.com
3 Functional Materials Department, Łukasiewicz Research Network—Institute of Non-Ferrous Metals, Sowińskiego 5, 44-100 Gliwice, Poland; lukaszh@imn.gliwice.pl
4 Department of Powder and Composite Materials, Łukasiewicz Research Network—Institute of Non-Ferrous Metals, Sowińskiego 5, 44-100 Gliwice, Poland; malgosia@imn.gliwice.pl
5 Faculty of Chemistry, Silesian University of Technology, Marcina Strzody 9, 44-100 Gliwice, Poland; szleperkasia@gmail.com
* Correspondence: mateuszc@imn.gliwice.pl; Tel.: +48-322380277

Received: 3 June 2020; Accepted: 22 July 2020; Published: 1 August 2020

Abstract: We have reported the synthesis of a new kind of composite combining a rhenium precursor and active carbon. Similarly to other refractory metals, rhenium exhibits several oxidation states that makes it an ideal candidate for redox-type energy storage materials. A simple impregnation of pretreated active carbon with ammonium perrhenate allowed to produce an electrode material with an enhanced specific capacitance. There was not any observed detrimental effect of metal species on the cycle life of the electrode. A small increase in charge transfer resistance was counter-balanced by the improved impedance in the whole examined range.

Keywords: active carbon; rhenium; supercapacitors; composite

1. Introduction

Supercapacitors are energy storage materials which can deliver a big amount of energy in a relatively short time, having a wide range of applications in consumer electronics, medical applications, start–stop systems with energy-regenerative braking, or power backup applications. World leading car manufacturers have started using supercapacitors in their commercial products, for example, the i-ELOOP system used in Mazda, which converts the vehicle’s kinetic energy into electricity as it decelerates, and uses it to control the audio system and air conditioning [1]. Start–stop systems, power-assisted steering, and braking in PSA Peugeot and Citroen and Lamborghini cars are powered by supercapacitors as well [2]. Samsung and Sony use supercapacitors for consumer electronics such as laptops, phones [3], tablets, cameras [4], and wireless sensors. Medical applications include patient monitoring systems, powered implants, fault applications, and various medical power backups [5]. Based on construction and operation, supercapacitors can be classified as electrochemical double layer capacitors (EDLC), hybrid supercapacitors, and pseudocapacitors [6]. EDLCs simply operate without redox reactions, while hybrid supercapacitors combine polarizable and non-polarizable (battery type) electrodes, and pseudocapacitors link carbon-based EDLC-type matrixes with a redox reaction material in the form of metal oxide or conducting polymers. In hybrid supercapacitors, electrodes are made of different materials, while in pseudocapacitors, the same material is used for the cathode and anode. The main advantage of pseudocapacitors is their significantly higher energy density in comparison...
with EDLCs. Metal oxide embedded in the carbon matrix may have a detrimental effect on the cycle life and power density, and therefore has to be used altogether with a porous host. Application of porous carbon facilitates the rapid access of electrolytes within the pores where metal oxide or metal hydroxide particles are anchored [7]. Different types of carbon materials have been considered for energy storage applications including active carbon, graphene, expanded graphite, graphite, carbon nanotube, and carbon gels. However, based on its availability, price, and properties, active carbon is suggested to be the most appropriate. The list of promising redox active compounds as either a metal oxide or metal hydroxide include nickel, cobalt, titanium, vanadium, ruthenium, molybdenum, manganese, and iron [8] as these metals are able to form varied valence states that result in a surplus of charge storage capacitance.

Within this paper, a combination of rhenium species and active carbon was examined. Rhenium, similarly to tungsten and molybdenum, has several different oxidation states and may form various compounds with oxygen atoms. The catalytic activity of rhenium was proved in the past. The activity of rhenium deposited on charcoal to catalyze cyclohexane and cumene dehydrogenation was examined in the late 1950s [9]. The catalyst was produced by sorption of ammonium perrhenate within charcoal in the presence of nitric acid with subsequent reduction with hydrazine hydrate and hydrogen gas. Rhenium is a catalyst component used in organic synthesis like alkylation and industrial processing including metathesis and reforming [10,11]. The combination of manganese and rhenium-modified activated carbon was studied as a catalyst in methanol decomposition, where rhenium facilitated the diversity of manganese ions [12]. Rhenium dispersed on the ordered mesoporous carbon was investigated as a catalyst for the reduction of aromatic nitro compounds to aromatic amino compounds, which can be used in drugs and pesticides production [13]. The rhenium-containing activated carbon catalyst can be also prepared using decacarbonyldirhenium and microwave irradiation [14]. Prior to the rhenium precursor, active carbon should be pretreated with nitric acid to produce active sites, responsible for rhenium binding. Short irradiation allows to decompose the rhenium precursor into metallic rhenium. Currently, the most common method to deposit rhenium on novel host materials like carbon nanotubes is chemical vapor deposition technology, utilizing decacarbonyldirhenium as a substrate [15]. However, decoration of multiwalled carbon nanotubes with rhenium can be performed using simple ultrasound mixing with perrhenic acid as well [16]. In recent years, an increase interest in rhenium can be observed, particularly regarding composite materials with the novel carbon materials family. Lithium and rhenium oxide can be also used as a so called pre-lithiation compound for activated carbon electrodes of lithium ion batteries [17]. Based on this concept, lithium is inserted into a positive electrode as mixed lithium rhenium (VII) oxide. Then, the battery cycling extracts the lithium from the positive electrode and moves towards the negative electrode. Extraordinary catalytic activity of rhenium has been recently found in graphene synthesis where rhenium substrate was responsible for conversion of the produced graphene layer to rhenium carbide [18]. In contrast to other metals, instead of carbides to graphene segregation, the opposite direction can be observed. In fact, this may help in lowering the possibility of second layer growth. A computational study by density functional theory showed high activity of a nanographene-rhenium complex in the electrocatalytic reduction of carbon dioxide to carbon monoxide [19].

2. Experimental

2.1. Materials Preparation

Active carbon (CWH-22, SGL Carbon Racibórz, Poland) was initially pretreated in 30% hydrogen peroxide in S/L ratio 1 g per 10 mL for 16 h. Carbon matrix with embedded oxygen-containing groups was dried in a desiccator over phosphorous pentoxide. This was used to avoid desorption of active species at temperatures higher than 100 °C. Active carbon and the product of its oxidation were labelled AC and AC-ox, respectively. Dry AC-ox was dispersed in demi water at 55 °C, and pH was set to 1.1 using nitric acid solution. Next, 5 g of ammonium perrhenate was added and the solution
was magnetically mixed for 2 h. An amount of 20 mL 40% hydrazine hydrate solution was used as the reducing agent for the rhenium precursor. The obtained rhenium-containing active carbon was denoted as AC-Re.

2.2. Characterization

Phase identification of AC, AC-ox, and AC-Re was examined using X-ray powder diffraction using Rigaku MiniFlex 600 with Cu Kα radiation, equipped with the silicon strip detector D/teX, and Soller slits 2.5”. Scanning electron microscopy (SEM) performed with Zeiss Leo Gemini 1525, equipped with secondary electron and backscattered electron detectors, was used to define materials’ morphologies. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method from adsorption data in a range 0.05–0.3. Pore size and pore volume distribution were calculated with the Barrett–Joyner–Halenda (BJH) method. Surface area and porosity were evaluated using 3Flex from Micromeritics in the relative pressure range 0.01–0.99, using nitrogen of purity 99.998%.

Electrochemical performance was tested using two electrode cell configurations in the Autolab PGSTAT 302/N workstation. Materials for electrodes (0.005 g) were mixed with poly (tetrafluoroethylene) and pasted on electrochemical nickel current collectors (25 mm diameter). Micro-glass fiber paper soaked with 6 M KOH was used as the electrode separator. The specific capacitance was calculated from a galvanostatic charge/discharge curve, and capacitance loss from cyclic voltammetry (CV) curves tested in the range 0–1 V with the scan rate 0.5 V/s. Electrochemical impedance spectroscopy (EIS), performed in the frequency range 100 kHz–100 mHz at 0 V with the amplitude of a sinusoidal voltage signal equal 10 mV was used to obtain Nyquist plots.

The specific capacitance was calculated from the galvanostatic charge/discharge curves using

\[ C_{SP} = \frac{i t}{m dU}, \]

where i is the current, t is the discharge time, m is the mass of active material of one electrode, and dU is the range of voltage. Additionally, specific capacitance was obtained from the CV curves used to evaluate cyclability. \[ C = \frac{1}{(E_2 - E_1)} \nu \int I(E) dE \] (integrated in boundaries from \( E_1 \) to \( E_2 \)),

while specific capacitance was calculated using \( C_{SP} = 2 C/m \), where \( E_1 \), \( E_2 \), \( \nu \), and \( m \) are the initial potential, final potential, scan rate, and mass of the active material of one electrode, respectively.

3. Results

The simple impregnation method followed by hydrazine hydrate reduction allowed to incorporate rhenium species within the oxidized active carbon matrix. The XRD method was used to analyze the possible phase changes during active carbon processing. Both active carbon and its oxidized form revealed two characteristic carbon signals around 26° and 42° (Figure 1). High intensity indicated its relatively good ordering; however, the increased width may be affected by the complexity of the amorphous and ordered domains. AC-ox showed signals slightly shifted towards lower angles mainly because of expanding the voids and pores by the oxygen-containing groups. Addition of ammonium perrhenate with subsequent reduction strongly ruined the ordered carbon domains but rhenium species were trapped within the carbon matrix. The obtained signals were attributed to ammonium tetraoxorhenate (VII) (DB card numer: 01-085-0346 based on PDF-2 Release 2020 RDB).

It was also found that application of a strong reducing agent such as hydrazine allowed for reducing the excessive oxygen-containing groups, while these combined with rhenium species were probably untouched. Therefore, no metallic rhenium was found within the structure.

SEM images showed the change in morphology of the parent active carbon and materials obtained after its oxidation and metal doping. Images were registered at magnification 5000× and 30,000×. It can be noticed that the starting active carbon was composed of various size particles with compact bigger blocks (Figure 2a,b). Oxidation of the carbon precursor broke and crushed bigger blocks, producing smaller particles debris (Figure 2c,d). Impregnation with ammonium perrhenate and hydrazine hydrate reduction induced partial corrugation of the smaller particles caused by desorption of the oxygen-containing groups. This process exerted a big pressure on the carbon structure, resulting in pore opening/damaging the
walls of the ordered pores structure (Figure 2e). The resulting rhenium-modified active carbon was very serrated (Figure 2f) or exfoliated (term used more appropriately for graphene-like materials).

As it was observed, the action of hydrogen peroxide and then hydrazine hydrate strongly changed the structure mainly by allowing access to newly developed pores. Therefore, it was important to determine the pores’ structures and the accessible specific surface area. For all samples, typical microporous adsorbent isotherms were obtained, with small hysteresis loops in all cases. It showed highly developed microporosity with hardly any observed mesoporosity (Table 1).

The oxygen-containing species in AC-ox strongly hampered the gas penetration, consequently decreasing surface area. These structural obstacles were partially mitigated by desorption during the composite reduction with hydrazine hydrate producing a carbon material with embedded rhenium species with a surface area close to that of the parent AC. Although a slight decrease in BET specific surface area was observed after the chemical treatment of the AC, the pore parameters were enhanced. An increase in pore volume for AC-Re was found regardless of the adsorption or desorption-based calculation.

Electrochemical characterization was performed mainly to define the specific capacitance and cyclability of the prepared electrode materials (Figure 3). The charge/discharge curves were recorded using the chronopotentiometry mode of the potentiostat at a current density ranging from 0.2 to 3 A/g. The specific capacitance calculated for AC, AC-ox, and AC-Re was 30, 37, and 57 F/g, respectively, all measured at 0.2 A/g. This showed that the pretreated carbon matrix with anchored rhenium species doubled the specific capacitance. The obtained GC/GD curve was ideally triangular with no iR drop observed in discharge mode. The presence of rhenium active species influenced the initial capacitance

Figure 1. X-ray patterns of the parent active carbon, the oxidized active carbon, and rhenium-modified matrix.

Table 1. Specific surface area and pore characteristics.

|         | BET Surface Area m²/g | BJH Pore Volume (Adsorption) cm³/g | BJH Pore Volume (Desorption) cm³/g | BJH Pore Size (Adsorption) Å | BJH Pore Size (Desorption) Å |
|---------|-----------------------|------------------------------------|------------------------------------|-----------------------------|-----------------------------|
| AC      | 1018.06               | 0.3068                             | 0.3024                             | 46.886                      | 48.144                      |
| AC-ox   | 984.10                | 0.2700                             | 0.2564                             | 42.739                      | 43.346                      |
| AC-Re   | 996.17                | 0.3416                             | 0.3332                             | 45.205                      | 46.896                      |
drop arising from the irreversible redox reactions between electrolyte and electrode. However, after 1000 cycles, some equilibrium in this aspect was observed and the specific capacitance drop at the end of the cycling tests was about 4.5%, similar for AC, AC-ox, and AC-Re. The parent AC withstood long cycling without any capacitance loss up to 800 cycles, then material deterioration was observed. The CV curves in all cases were of acceptable shape but for AC-ox and AC-Re, shorter edges were observed, i.e., quicker and faster charging and discharging. This was probably combined with the improved wettability and consequently easier penetration of the pore structure by the electrolyte.

Figure 2. SEM images at magnification 5000× and 30,000× obtained for parent active carbon (a,b), oxidized active carbon (c,d), and rhenium-modified active carbon (e,f).
Figure 3. Cont.
Figure 3. Set of electrochemical data including (a) cyclic voltammetry (CV) curves at a scan rate of 500 mV/s; (b) galvanostatic charge/discharge tests at a current density of 0.2 A/g; and (c) Nyquist plots.

The imaginary vs. real impedance relations, which can be seen in the Nyquist plots, were significantly steeper for AC-Re with a lower solution resistance value (zoomed high-frequency region). Consequently, penetration of the carbon pores was enhanced by rhenium species doping. The calculated charge transfer resistance was 0.07, ~0.10, and 0.06 Ω for AC, AC-ox, and AC-Re, respectively. It should be emphasized that the low-frequency region was significantly scattered for AC-ox. The semi-circle, which can be observed typically for pseudcapacitive materials, was very small in AC-Re. This is a consequence of the reduction of most oxygen species by hydrazine, therefore the redox reactions are combined only with rhenium species rather than residual oxygen groups.

4. Conclusions

The active carbon/rhenium species composite has been successfully synthesized from commercial active carbon and ammonium perrhenate by the facile wet impregnation method followed by chemical reduction. Rhenium species were anchored in the form of ammonium perrhenate, while the reducing agent was used to remove residual oxygen species within the oxidized carbon matrix. Significant improvement in the specific capacitance with a high cyclability was found.

Author Contributions: Conceptualization, M.C.; methodology, M.C., A.K.; formal analysis, Ł.H., M.O., M.C.; investigation, K.S., M.C. A.K.; resources, M.C., A.K.; writing—original draft preparation, M.C., M.D.; writing—review and editing, M.C., M.D.; visualization, M.D.; funding acquisition, M.C. All authors have read and agreed to the published version of the manuscript.

Funding: This work was funded by a statutory grant from the Łukasiewicz Research Network—Institute of Non-Ferrous Metals in Gliwice, Poland, entitled: Modification of selected carbon materials with rhenium species, grant number; 0332029008.

Conflicts of Interest: On behalf of all authors, the corresponding author states that there is no conflict of interest.
References

1. Mazda ‘i-ELOOP’ Capacitor-Based Brake Energy Regeneration System. Available online: https://www2.mazda.com/en/publicity/release/2011/201111/111125a.html (accessed on 15 January 2020).
2. Automotive. Available online: https://www.maxwell.com/solutions/transportation/auto (accessed on 15 January 2020).
3. Samsung Galaxy Note 9 Review: This is Power User Perfection. Available online: https://www.sammobile.com/samsung/galaxy-note9/review/ (accessed on 15 January 2020).
4. Boscaino, V.; Capponi, G.; Marino, F. Experimental test on a fuel cell—Supercapacitor hybrid power supply for a digital still camera. In Proceedings of the 2009 44th International Universities Power Engineering Conference (UPEC), Glasgow, UK, 1–4 September 2009.
5. Meng, C.; Gall, O.Z.; Irazoqui, P.P. A flexible super-capacitive solid-state power supply for miniature implantable medical devices. *Biomed. Microdevices* **2013**, *15*, 973–983. [CrossRef] [PubMed]
6. Najib, S.; Erdem, E. Current progress achieved in novel materials for supercapacitor electrodes: Mini review. *Nanoscale Adv.* **2019**, *1*, 2817–2827. [CrossRef]
7. Zhao, B.; Chen, D.; Xiong, X.; Song, B.; Hu, R.; Zhang, Q.; Rainwater, B.H.; Waller, G.H.; Zhen, D.; Ding, Y.; et al. A high-energy, long cycle-life hybrid supercapacitor based on graphene composite electrodes. *Energy Storage Mater.* **2017**, *7*, 32–39. [CrossRef]
8. Nguyen, T.; de Fátima Montemor, M. Metal Oxide and Hydroxide–Based Aqueous Supercapacitors: From Charge Storage Mechanisms and Functional Electrode Engineering to Need-Tailored Devices. *Adv. Sci.* **2019**, *6*, 1801797. [CrossRef] [PubMed]
9. Balandin, A.A.; Karpeiskaya, E.I.; Tolstopyatova, A.A. Catalytic properties of rhenium. Communication 1. Rhenium as dehydrogenation catalyst, Bulletin of the Academy of Sciences of the USSR. *Bull. Acad. Sci. USSR Div. Chem. Sci.* **1959**, *8*, 1318–1324. [CrossRef]
10. Mol, J.C. Industrial applications of olefin metathesis. *J. Mol. Catal. A Chem.* **2004**, *213*, 39–45. [CrossRef]