

COAL CHAR AS A SUBSTITUTE FOR NATURAL GRAFITE

MIHAI CRUCERU, BOGDAN DIACONU

Constantin Brâncuși University of Târgu Jiu, Romania

ABSTRACT : The paper briefly presents the project “*Coal char as a substituting material of natural graphite in green energy technologies*” - CHARPHITE that it is implemented by a research team from University “Constantin Brancusi” and the partial results.

KEY WORDS (TNR 10 pt Bold): Insert keywords .

1. INTRODUCTION (Title of chapter TNR 14 pt Bold)

In response to recent demand increases caused by emerging technologies, the European Commission (EC) established the Raw Materials Initiative to limit the

impact that material supply shortages may have on the European economy. In the study released by the EC assessing materials in critical demand , natural graphite was identified as exhibiting a high supply risk and high economic importance (Fig. 1).

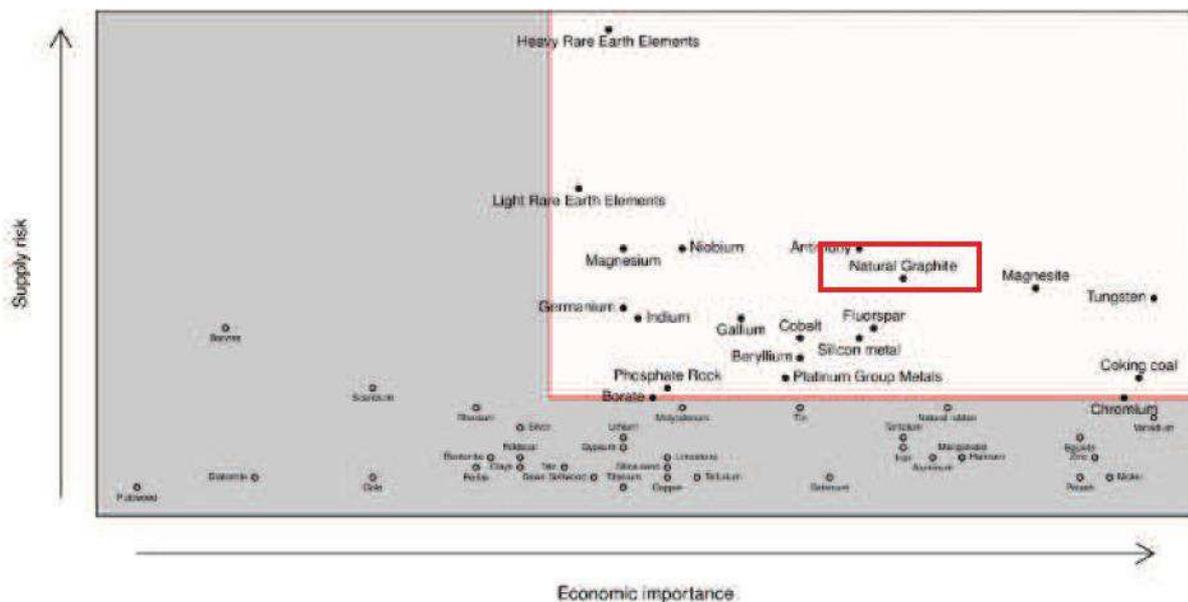


Figure 1. Plot of twenty critical raw materials identified as critical from the list of fifty-four candidate materials (http://ec.europa.eu/enterprise/policies/raw-materials/critical/index_en.htm)

Two main pathways generate graphitic carbon on Earth:

- (i) carbonization–graphitization of organic matter derived from living organisms [1]
- (ii) precipitation from deep fluids saturated in carbon-bearing molecular and ionic species [2]

Natural well-crystallized graphite is rare and, instead, a poorly crystallized, disordered material commonly called “graphitic carbon” occurs in many geological and environmental settings. China is responsible for nearly 80% of graphite produced worldwide, followed by Brazil, Canada, India and European countries. [3] Noticeably, human activity also generates graphitic carbon, like char.

Three types of graphite are mined for commercial use [2]:

- (i) vein/lump (generally pure and perfectly crystallized graphite,
- (ii) flake (graphite crystals, $>100\ \mu\text{m}$
- (iii) amorphous/microcrystalline graphite grains ($<1\ \mu\text{m}$).

In all cases, purification for commercial use consists of milling in an aqueous slurry, followed by flotation to separate graphite from its mineral matrix. Further treatment may involve acid treatment (HCl and/or HF), sometimes followed by high temperature heating.

Graphitic carbon exhibits a large range of structures (e.g. amorphous-like compounds, turbostratic structures, to crystalline graphite), and graphite and well-ordered graphitic carbon exhibit a huge structural anisotropy, with strong consequences for physical properties. For instance, electron delocalization in graphene layers yields a high in-plane electrical conductivity equivalent to that of metals. Perpendicular to layering, however, conductivity is so low that graphite is an insulator parallel to its c-axis. Other remarkable bulk properties of graphite and some synthetic graphitic carbon include a high thermal conductivity, a high sublimation point (ca $3825\ ^\circ\text{C}$ at atmospheric pressure), a low thermal expansion coefficient, and a relatively low density (ca. 2.1–2.3).

Crystalline graphite is also highly refractory and chemically inert, whereas the chemical reactivity of graphitic carbon increases with structural disorder and the abundance of chemical impurities.

2. GRAPHITIZATION

The structure and chemistry of graphitic carbon that can form during the graphitization process have been studied extensively in materials science, because of the potential industrial applications of graphitic carbon. [4] The formation of graphite from organic molecules is a high-temperature (ca. $3000\ ^\circ\text{C}$) [6] two-stage process [7]: (1) carbonization, which eliminates most noncarbon components and initiates formation of an aromatic skeleton consisting of a network of six-membered, planar rings of carbon; followed by (2) graphitization *sensu stricto*, which consists mostly of polymerization and structural rearrangement of the aromatic skeleton towards the thermodynamically stable ABAB layered sequence of graphite [4].

Changes of properties during graphitization starts at temperatures of about $1500\ ^\circ\text{C}$ and continues to about $2200\ ^\circ\text{C}$, the temperature limit that ends the graphitizing process being $2500\text{--}3000\ ^\circ\text{C}$. Graphitization produces essential changes in carbon structure that over $2000\ ^\circ\text{C}$ passes into the crystalline state. This involves altering the characteristics of structure, thermal and mechanical resistance, density (porosity), resistivity and chemical stability, values influenced by the nature and composition of raw materials and temperature level reached. [8,9].

Since it results from a high-temperature process, coal combustion carbon-rich solid residue (or CHAR) included in coal combustion ash is one of the most promising materials for substituting natural graphite through the graphitization process. [10–12] However, in addition to the treatment temperature, the characteristics of the precursor materials, the mineral matter [13,14] and the carbon microtexture [5, 15–18] also influence the graphitization process. These factors ultimately determine the quality of the graphite, and consequently its

application, as well as the final cost. Therefore, there is interest in developing further research on structural ordering and crystallinity of alternative graphite precursors, and moving the scope of the research from bulk sample analysis to the study of the effect of the heat treatment graphitization at a microscopic level.

Fly ashes (FAs) are the major coal combustion residues produced at high temperature (1300–1500 °C) in boilers. Their composition and properties depend on prevailing inorganic and organic constituents, making fly ashes a very complex geomaterial for investigation, i.e. the determination of its composition (organic and inorganic components), granulometry, dominant particle morphologies and other properties. [19-23] In particular, Unburned Carbon concentrates from high-rank coal fly ashes may show carbon contents of >90%, a high degree of turbostratic structural order, and a lamellar microtexture. Such a lamellar microtexture, specifically when there is a preferential planar orientation of the polyaromatic basic structural units (BSUs), was reported to be the most graphitizable carbon [6,7,30,31]. In addition, metallic species are able to act as catalysts during the high temperature treatment. On this basis, Unburned Carbon in fly ashes is a potential precursor for Graphitized Carbon, with suitable structural characteristics to be employed in industrial applications. Rouzaud and Oberlin [6] obtained carbon materials with a high degree of structural order CHAR, as reflected by the evolution of the XRD and Raman crystalline parameters.

HRTEM-EDS analysis also demonstrated that this high degree of structural order in CHAR was mainly due to the presence of iron and silicon in the precursor fly ash carbons. [9,10] The evolution of the corresponding anisotropy parameters (structure and texture) may also be analyzed via optical microscopy and high resolution analytical techniques (such as SEM, TEM, EDS, XRD, Raman spectroscopy, etc.), and correlated with some properties, physical structures, and degree of

graphitization achieved in the prepared materials. [16]

Due to the climate change and depleting of petroleum supplies, the research and development of clean energy is of crucial importance in next decades. Many advanced technologies for clean energy conversion, for example fuel cells, water electrolysis, metal-air batteries, and CO₂ to fuel conversion, are the subject of both fundamental and applied research. [24] The core of these energy conversion technologies is a series of electrochemical reactions, which include electrocatalytic oxygen reduction reaction (ORR) and hydrogen oxidation reaction (HOR) that occur on the cathode and anode of a hydrogen–oxygen fuel cell, respectively; and hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) at the cathode and the anode of an electrolytic cell producing gaseous molecular hydrogen and oxygen, respectively. [25] However the kinetics of these electrochemical processes significantly influences the output performance of the aforementioned clean energy conversion devices. The most critical problem is how to effectively catalyze these reactions to achieve as low over potential and high current density as possible. The kinetics of two electron transfer in half-cell HER and HOR is rapid, but the four electrons-four protons associated with electron transfer in ORR and OER is kinetically slow. Currently, the poor catalytic performance of the cathodic ORR electrode is the major cause of efficiency reduction in the case of proton exchange membrane fuel cells (PEMFC). [25]

All these reactions started to be catalyzed by precious metals such as platinum (Pt), iridium (Ir) and ruthenium (Ru)-based catalysts which allowed high catalytic activity. [26, 27] However, they are scarce and high priced, which limit their large-scale applications in these relevant clean energy technologies. In this regard, the development of novel electrocatalysts with high catalytic activity, longer durability, lower cost, scalability could greatly facilitate the improvement of clean energy infrastructures. Consequently, in the past few years, novel electrocatalysts such transition metals

(oxides) combined with different types of carbon materials and non-metal carbon-based materials (doped carbons - N, B, O, S, P) have been explored as alternatives of precious metal electrocatalysts. [28] Within carbon materials, graphitized chars, their exfoliated products and metal oxide composites to be prepared in this project, emerge as excellent alternative electrocatalysts for the referred electrochemical energy-related reactions.

3.PROJECT OBJECTIVE

The project aims to demonstrate, by a detailed fundamental and applied investigation, the technical feasibility to utilize fresh and reclaimed landfilled CHAR derived from fly ash and bottom ash as a substitute for graphite based materials in green energy applications. The proposed approach, demonstrates innovative methods/technologies to develop recovery processes and transform CHAR from coal ash into a high-grade, high-value material with various application. This creates the possibility for the substitution of natural graphite. The project expects to achieve results to be used as an initial basis for the advanced, waste-less and environmentally safety utilization of various coal combustion ashes to obtain char concentrates, and to use them as a precursor material to produce exfoliated heteroatom-doped products and composites with metal oxides, for applications as catalysts in electro-assisted reactions for sustainable energy production: hydrogen evolution reaction (HER), oxygen evolution reaction (OER), oxygen reduction reaction (ORR) for fuel cell technology and water splitting (simultaneous O₂ and H₂ production).

The project also has a secondary objective related with the assessment of natural graphite occurrences and sampling in the consortium countries for the characterization of their technologic properties, for comparison with the CHARS and graphitized CHARS produced under the project main objectives. The output would be an assessment of the viability of future work including those natural graphite, or the protection thereof for future generations by

the substitution with the CHAR graphite product.

Other scientific derivative objectives are:

- Selection and characterization of fresh and landfilled coal ash identified as suitable secondary raw material to be used for graphite supply and natural graphite substitution;
- Data articulation and integration for the optimization of the CHAR recovery methods and technologies to maximize the CHAR recovery, and to increase the CHAR quality in relation to its utilization, i.e. by optimizing the removal of the unrequired inorganic content;
- Data articulation and integration for the optimization of the iron-rich morphotype recovery methods and technologies to maximize their recovery at high purity levels, to increase “a priori” the quality of these iron concentrates in relation to its utilization as metallic oxides to be incorporated in graphite in electro-assisted reactions;
- Assessment of techno-economic feasibility of the proposed separation/recovery processes taking into consideration the remaining inorganic residues and their potential utilization;
- Obtain char concentrates, as direct and indirect (via graphitization) precursors/new materials for graphite substitution in green high-tech energy solutions;
- Apply and validate the main driving parameters of the innovative technology in the laboratory experimental flow for new precursors/products manufacturing, based on the most promising starting fly ash/bottom ash/char as raw materials;
- Prove the feasibility of conserving natural graphite, and reducing European Union, Argentina and South Africa dependency based on the evaluations carried out in the networking countries, including collecting data, inventory and mapping of site/dumps location, production for sustainable development;
- Obtain a detailed characterization of the natural graphite deposits/occurrences in

the networking countries for reassessment of old information, and compare to CHAR derived graphite, to enable fundamental political decisions regarding sustainability for future generations;

- Promote a fast and environmentally friendly way to obtain large amounts of graphitic material, and at the same time to increase the substitution of natural graphite utilization in green energy technologies, and to contribute to increase the recycling of coal combustion ashes.
- Utilization of the CHAR graphitic material to produce exfoliated heteroatom doped products and composites with metal oxides, for application as catalysts in electro-assisted reactions for energy applications: hydrogen evolution reaction (HER), oxygen evolution reaction (OER), oxygen reduction reaction (ORR) for fuel cell technology, and water splitting (O₂ and H₂ simultaneous production).

4.PARTIAL RESULTS

In the first stage - Selection and characterization of fresh and landfilled coal ash identified as suitable secondary raw material to be used for graphite supply and natural graphite substitution – UCB collected over 100 kg of bottom ash from each landfill from Turceni, Rovinari and Govora of which 300 samples were formed.

We have started the characterization of the samples and partial results are shown in table 1.

Table 1. Sample characterization – partial results

Particles size	Percent	A ^a	V ^a	C _{fix} ^a
mm	%	%	%	%
> 4	1,5	-	-	-
2 - 4	2,4	72.30	13.36	14.34
1 - 2	4,2	75.75	8.24	16.01
0.5 - 1	8,6	82.60	6.61	10.79
0.25 - 0.5	16,1	92.94	4.41	2.65
0.125 - 0.25	22,6	96.65	2.99	0.36
0.09 - 0.125	11,3	97.43	2.59	0.02
0.063 - 0.09	9,4	97.49	2.51	-
< 0.063	23,9	96.94	3.06	-

5.CONCLUSION

The project aims to demonstrate, by a detailed fundamental and applied investigation, the technical feasibility to utilize fresh and reclaimed landfilled CHAR derived from fly ash and bottom ash as a substitute for graphite based materials in green energy applications.

The partial results demonstrate that the ash resulted from coal combustion in the power plants from Oltenia contains unburned coal, especially the large particles, of 0.5 - 4 mm diameter.

Acknowledgment: This work was supported by a grant of the Romanian National Authority for Scientific Research and Innovation, CCCDI-UEFISCDI, project number ERAMIN-CHARPHYTE-2, contract no 15/2016, within PNCDI III

REFERENCES

- [1] Buseck PR, Beyssac O, 2014. Elements 10, 421-426;
- [2] Rumble D, 2014. Elements 10, 427-433;
- [3] Barthélémy et al., 2012. Bureau de Rech. Géol. Minières, BRGM/ RP-61339-FR, 91

- pp.; [4] Beyssac O, Rumble D, 2014. Elements 10, 415–420;
- [5] Burgess-Clifford et al., 2009. Fuel Proc. Technol. 90, 1515-1523;
- [6] Rouzaud JN, Oberlin A, 1989. Carbon, 27, 517-529;
- [7] Oberlin A, 1989. Chemistry and Physics of Carbon 22. Marcel Dekker, New York, pp 1-143;
- [8] Panaitescu C, Predeanu G., 2010. Revue Roumaine de Chimie 55 301-310;
- [9] Predeanu et al., 2015, Int. J. Coal Geol. 139, 63-79;
- [10] Cabielles et al., 2008. Energy Fuels 23, 942-950;
- [11] Cabielles et al., 2009. Energy Fuels, 23, 942-950;
- [12] Tai et al., 2009. J. Raman spectroscopy 41, 933-937;
- [13] Pappano PJ, Schobert HH, 2009. Energy & Fuels 23, 422-428;
- [14] Rodrigues et al., 2012. Int. J. Coal Geol. 93, 49-55;
- [15] Duber et al., Extend Abstracts, 21st Biennial Carbon Conf., 1993; pp 316–317;
- [16] Suarez-Ruiz I, Garcia AB, 2007. Energy Fuels, 21, 2935-2941;
- [17] Rodrigues et al., 2011. Int. J. Coal Geol. 87, 3-4: 204-211;
- [18] Rodrigues et al., 2011. Int. J. Coal Geol. 85, 2: 219-226;
- [19] Vassilev SV, Vassileva CG, 2007. Fuel 86, 1490-1512;
- [20] Ward CR, 2002. Int. J. Coal Geol. 50, 135-168;
- [21] Hower et al., 1995. Proc. 11th Int. Coal Testing Conf., Lexington, 10-12, 49-54;
- [22] Hower et al., 2005. Energy Fuels 19, 653-655;
- [23] Bailey et al., 1990. Fuel 69, 225-239;
- [24] Benson et al., 2009. Chem. Soc. Rev. 38, 89–99;
- [25] Wolfschmidt et al., 2010. Fuel Cell Science, John Wiley & Sons, Inc., pp. 1–70;
- [26] Debe MK, 2012. Nature, 486, 43–51;
- [27] Strasser P, 2013. Electrocatalysis, Wiley-VCH Verlag GmbH & Co. KGaA, pp. 259–292;
- [28] Antolini E, 2014. ACS Catal., 4, 1426–1440;