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THERMAL GRAVIMETRIC ANALYSIS OF GENERAL-GRADE GRAPHITE, GLASSY, PREBAKED AND PYROLYTIC CARBONS

TERMOGRAWIMETRYCZNA ANALIZA ELEKTROD WĘGLOWYCH

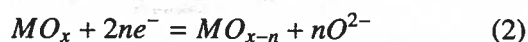
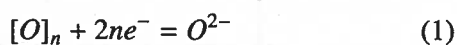
An investigation of the thermal oxidation resistance of various carbon materials has been performed via thermal gravimetric analysis (TGA). Experiments were conducted for general grade graphite, glassy, prebaked and pyrolytic compact solid-body carbon samples. The loss of mass for each carbon sample was measured as a function of a temperature in the presence of several flowing gases. An isothermal heating was also performed for each carbon sample, at 560°C, in flowing air. This work is beneficial for the novel FFC (Fray-Farthing-Chen) — Cambridge electro-reduction process, in which carbon materials are currently employed as anodes in a high temperature molten salt electrolytic cell. It is therefore desirable to establish the inertness and resistance of such materials in the presence of anodically active oxygen. Such information is advantageous as it may serve to minimise operating costs, increase cell efficiency, and ensure a lower contaminated cathodic product. The studies prove that glassy and pyrolytic carbons are the most resistance to oxidation. However, it is not recommended that any of the tested carbon-based materials should be used as anodes at temperatures in exceeding of 625°C. This is due to a significant loss of mass attributed to high oxidation rates and the formation of carbon oxides (CO_x).

Keywords: carbons, thermal analysis (TGA), FFC-Cambridge process

Przedstawiono wyniki badań utleniania elektrod węglowych wykorzystując technikę analizy termicznej (TGA). Badano ubytek masy próbek w trakcie liniowego wzrostu temperatury, jak również podczas izotermicznego ogrzewania (560°). Analizowane elektrody węglowe mają zastosowanie w procesach redukcji FFC (Fray-Farthing-Chen) — Cambridge. Spełniają rolę anod w wysokotemperaturowym procesie elektrolitycznym. Istotne jest aby takie elektrody wykazywały bierność i opór w obecności tlenu. Dobór odpowiednich elektrod pozwala zmniejszyć koszty operacyjne procesu i mniejsze zanieczyszczenie produktu katodowego. W niniejszej opracowaniu przedstawiono wybrane wyniki badań termogravimetrycznych i badań strukturalnych.

1. Introduction

A novel molten salt process for producing metal (M) directly from its metal oxides (MO) was discovered in 1997, by researchers at the University of Cambridge. The process was named the FFC (Fray-Farthing-Chen) — Cambridge process. It was proposed that metal oxides or metal-oxygen solid solutions could be electrochemically reduced through a route termed electrodeoxidation [1,2]. The mechanism involves the ionisation of oxygen from a cathodically polarised metal oxide.



The oxygen anion passes through a molten salt electrolyte, usually CaCl₂ (melting point 762°C) at 900°C

[2]. The anion is then discharged as oxygen gas on an inert anode [3]. Various forms of carbons have been typically used as the anode in this process to date. These include general-grade graphite, glassy, prebaked and pyrolytic carbons. The key factors influencing their selection as anodes include: their physical stability at the operating temperature (sublimes at 3500°C), their resistance to molten salt attack, their low electrical resistivity, their low cost; their ease of deployment; and their resistance to thermal shock [4-6].

However, limited quantitative information is available into the thermal oxidation resistance of these particular carbons. It is therefore important to determine the actual temperature threshold at which an unacceptable level of oxidation occurs for these forms of carbons, and also which of these carbons has the highest oxidation resistance relative to one another. This would serve

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to establish the maximum operating temperature of the electrolytic cell (for each of the tested carbon materials), so that any formation of carbon oxides (CO_x) and subsequent mass loss is kept at an acceptable rate; and also indicate which of the tested carbon materials is the most suitable for use as an anode in the FFC-Cambridge process. This work may ultimately result in: lower operating costs; less labour time; reduced cell downtime since the carbon anode would need less frequent replacing; higher cell current efficiencies as potential back-reactions from the formed carbon-oxides will be minimised; and higher purity metallic product due to less carbon contamination [7]. Also, environmental benefits may be obtained due to reduced greenhouse gas emissions, since oxygen could be generated in place of carbon oxides.

2. Materials and experiment

General-grade graphite, glassy, prebaked and pyrolytic carbons have been commonly used as anodes at a laboratory scale for the FFC-Cambridge process. These carbons fall into a class of graphite-based allotropes, in which layers of hexagonally arranged carbon atoms are bound by sp^2 orbitals, and are stacked in parallel through delocalised π electron clouds [8]. The delocalised electrons between each planar layer account for the conductivity of graphite-based carbons.

General-grade graphite is produced through graphitisation of baked carbon, by heat treating the material at temperatures between 2600-3300°C. This high temperature causes the pre-ordered carbon structure to become highly ordered over large areas. This results in the cleavage of graphite being perfect in one direction. General-grade graphite was obtained from Tokai Carbon Europe, it was Tokai HK-40.

Glassy carbons or „amorphous” carbons are produced through pyrolysis of thermosetting resins (e.g. phenol-formaldehyde) under a controlled heating rate to high temperatures. They have a highly disordered structure and glass-like features, such as high hardness, being brittle, and a low permeability to gases [9]. Unlike general-grade graphite, the carbon atom layers are not distributed regularly over its area. This disordered structure prevents it from forming intercalation compounds, which accounts for its very high resistance to corrosion by acid or alkaline melts. Glassy carbon samples were obtained from HTW GmbH.

Mixing produces prebaked carbons and compacting ground calcined petroleum coke with petroleum pitch. The petroleum pitch essentially binds the mixture into the required shape. The resulting mass is then furnace-baked over several weeks to a temperature of 1250°C. These results in the pitch being carbonised,

ensuring a solid bond is created between the calcined petroleum coke particles [10]. Also, prebaked carbons unlike the other selected carbons require no further heating, and are thus classified in a category of carbons called mesomorphous.

Pyrolytic carbons are formed through the deposition of successive carbon layers from hydrocarbon gases. The characteristics of pyrolytic carbons are similar to glassy carbons, including fragility, closed micro-porosity, and very high resistance to chemical agents. It has a crystal structure that is highly disordered over large areas. Pyrolytic carbon samples of variant V25 were obtained through Carbone Lorraine18. This specific variant was treated at a temperature of 2500°C.

Recording of TG and DTA curves for the samples heated in the air or nitrogen were performed using TA Instruments Universal Analysis 2000. The obtained thermoanalytical diagrams referred to the samples of 10 mg to 20 mg masses. At first experiments a 5°C/min heating rate was applied within the temperature range from 20 to 1000°C.

An isothermal oxidation test was also performed for 12 hours, in flowing air, at 560°C. The primary reason for selecting this particular temperature is that it may be possible to conduct electroreduction experiments, at this working temperature in NaCl-CaCl₂ eutectic salt mixtures (melting point ~ 500°C at 50:50 mol%) [11]. It is therefore worthwhile to investigate the inertness of the various carbon samples in the presence of oxygen at this reduced temperature (with a 60°C stability clearance).

3. Results and discussion

Fig.1 shows TG curves of oxidation of all carbon materials in the air. It is noticeable that glassy and pyrolytic carbons have the highest resistance to oxidation, of the all carbon materials tested.

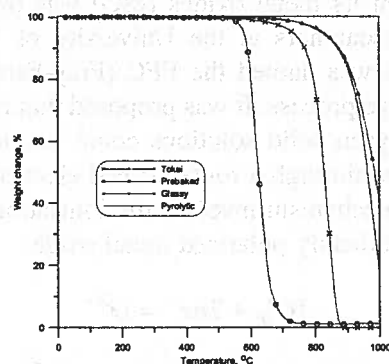


Fig. 1. TG curves (loss of mass) for linear heating all carbons in the air

Both these forms of carbon retain more than 99.0% of their original mass, up to temperature of 700°C, when

a constant 5°C/minute heating-rate is applied. This temperature is about 100°C higher than for general-grade graphite, and more than 150°C higher than for prebaked carbon, in which the same amount (99.0%) of the material's original mass is retained.

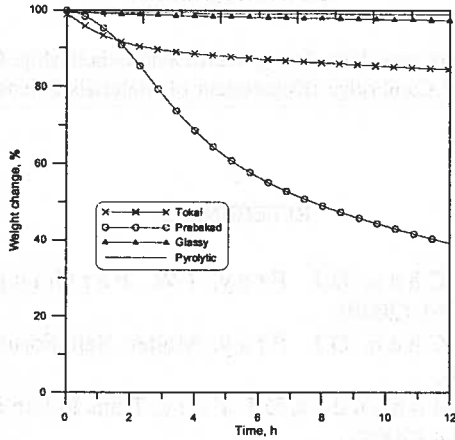


Fig. 2. TG curves during isothermal oxidation all carbons in air for 12 hours

Glassy and pyrolytic carbons are also the best out of the tested carbons at an isothermal temperature of 560°C as seen in Fig. 2. They both appear to be relatively inert in the presence of flowing air at this temperature, maintaining more than 97.0% of their original weight up to 12 hours. Therefore it is beneficial to use glassy and pyrolytic carbons as anodes for FFC-Cambridge electro-reduction process, if the electrolysis is carried out at the lower temperatures than conventionally used. That may be possible by using eutectic salt mixtures, as NaCl-CaCl₂, which would allow a working cell temperature of 560°C. However, such a reduced temperature could significantly lower an electro-reduction rate. This disadvantage may be offset by benefits such as reduced cathodic product contamination, and higher cell-efficiencies due to minimisation of possible back-reactions involving salt and carbon oxides. Cell downtime could be reduced as less frequent replacement of anode electrodes is required. Furthermore, it may even be possible that glassy and pyrolytic carbons can anodically generate oxygen gas, due to their relative inertness with oxygen at such relatively low temperatures.

The studies confirmed that 700°C, is the Maximum Advisable Temperature Limit (MATL) for glassy and pyrolytic carbons. At the higher elevated temperatures it is likely that these particular carbons would lose too much their mass if exposed to oxygen for significant time periods (i.e. > 24 hours). Therefore, further isothermal tests must be conducted at the temperatures greater than 700°C to support this assumption. It should be noted that the MATL of 700°C for glassy and pyrolytic carbons,

would be lowered in the salt environments. This is due to salt catalytic effects on the carbon-oxide formation, and is relevant for the FFC-Cambridge process in which molten salts are used.

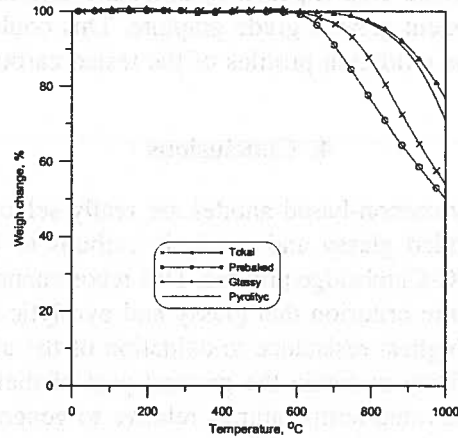


Fig. 3. TG curves (loss of mass) for linear heating all carbons in the nitrogen atmosphere

Fig. 3 shows TG of different carbon materials during heating in the nitrogen. The carbon samples tested were assumed to fully retain their original mass, with elevating temperatures, in the presence of these „inert“ gases. This assumption was based on the fact that carbon does not react with nitrogen gas, until temperature of at least 1700°C [12]. Therefore the loss of mass seen in Fig. 3 is certainly attributed to the trace amounts of oxygen, found in the nitrogen gas cylinders, supplied by Air Products (1ppm).

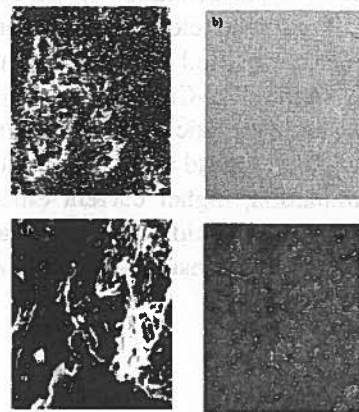


Fig. 4. SEM pictures: a) general grade graphite; b) glassy carbon; c) prebaked carbon; d) pyrolytic carbon. Each SEM image slide dimension corresponds to a length of 100µm (JSM 5400LV-JEOL)

It is likely that apart from differences in crystal arrangements, a reason for pyrolytic and glassy carbons performing better than general-grade graphite and prebaked carbon may be due to differences in their surface properties (Fig.4).

It can be seen that glassy and pyrolytic carbons have the least surface defects out of the four carbons tested. Their smooth surface ensures that a relatively low surface area is available for reaction with oxygen, unlike the higher surface area exposed by prebaked carbon and to a lesser extent general grade graphite. This could partly explain the oxidation profiles of the tested carbons.

4. Conclusions

If any carbon-based anodes are really selected it is recommended glassy and pyrolytic carbons to be used for the FFC-Cambridge process. This recommendation is based on the criterion that glassy and pyrolytic carbons have the highest resistance to oxidation of the all tested carbons. They maintain the greatest part of their initial mass at elevated temperatures, relative to general-grade graphite and prebaked carbon. At temperatures in exceeding of 700°C, glassy and pyrolytic carbons become highly reactive with oxygen. This is supported by TGA experiments conducted in nitrogen gas, containing trace amounts (ppm-level) of oxygen. Although that gas, if pure, should not react with carbon, significant oxidation and mass loss still occurred at 700°C for the selected carbons. This mass loss was attributed to the carbon reacting with trace amounts of oxygen impurities in the relevant inert gases, demonstrating how reactive carbon and oxygen are at such temperatures. It is therefore highly unlikely that at 900°C, (the conventional operating temperature of the FFC-Cambridge process), any carbon-based anodes will remain sufficiently inert, even in the presence of small quantities of oxygen.

However, if eutectic electrolyte systems, such as NaCl-CaCl₂ melts are used at operating temperatures close to 560°C, in the FFC-Cambridge process, it is possible that glassy and pyrolytic carbons remain sufficiently inert when used. This should result in minimised cathode product contamination, higher current efficiencies (due to less salt and carbon oxide reactions), and less cell down-time in replacing consumed anodes. A significant

level of oxygen synthesis may also be possible for carbons at such reduced temperatures, but this requires the further exploratory work.

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REFERENCES

- [1] G.Z. Chen, D.J. Fray, T.W. Farthing, *Nature* **407**, 361 (2000).
- [2] G.Z. Chen, D.J. Fray, *Molten Salt Forum* **7**, 159 (2000).
- [3] K.S. Mohandas, D.J. Fray, *Trans Indian Inst. Met.* **57**, 584 (2004).
- [4] G.S. Brady, H.R. Clauber, *Materials Handbook*, McGraw-Hill 131 (1997).
- [5] C.W. Forsberg, P.F. Peterson, *International Congress on Advances in Nuclear Power Plants (ICAPP '04)* 4152 5 (2004).
- [6] H.H. Uhlig, *The Corrosion Handbook*, John Wiley and Sons Inc, London 350-351 (1948).
- [7] R.O. Suzuki, K. Teranuma, K. Ono, *Metallurgical and Materials Transactions B* **34B**, 293 (2003).
- [8] M. Inagaki, *New Carbons: control and structure of functions*, Elsevier, Oxford 6 (2000).
- [9] A.A. Peric-Grujic, O.M. Neskovic, M.V. Veljkovic, M.D. Lausevic, Z.D. Lausevic, *J. Serb. Chem Soc* **67**, 761 (2002).
- [10] W.T. Choate, J.A.S. Green, *U.S. Energy Requirements for Aluminum Production: Historical Perspective, Theoretical Limits and New Opportunities*, Prepared under contract to: BCS Inc. Columbia MD 31 (2003).
- [11] E.M. Levin, C.R. Robbins, H.F. McMurdie, *Phase Diagrams for Ceramists*, American Ceramic Society Inc Supplement 302 (1969).
- [12] L.L. Shreir, *Corrosion 2 — Corrosion Control*, Haynes Butterworth, London (1976).