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POROUS CARBON ANODES FOR THE SUPPLY OF METHANE DURING ELECTROWINNING OF ALUMINIUM

Babak Khalaghi¹, Henrik Gudbrandsen², Ole Sigmund Kjos², Karen Sende Osen², Tommy Mokkelbost², Geir Martin Haarberg¹

¹Department of Materials Science and Engineering, Norwegian University of Science and Technology (NTNU), NO-7491, Trondheim, Norway

²Sintef Materials and Chemistry, Trondheim 7465, Norway

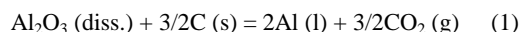
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Abstract

One of the major downsides of the current aluminium production process is the high amount of CO₂ emission. One alternative is to replace the consumable carbon anodes with inert anodes so that oxygen evolves instead of CO₂ and PFC emissions. However, so far a sufficiently inert anode has not been found. Another option is to utilize natural gas through porous anodes. This will decrease CO₂ emission remarkably and also eliminate PFC emissions and anode effect. The porous anode could be made of carbon or it can be inert. However, the as-mentioned problem still exists regarding porous inert anodes. Therefore, at the moment porous carbon anodes seem to be the best practical option. In this study, porous anodes made of different grades of graphite were used for electrolysis experiments. Also, off-gas analysis was performed to get an insight of the ongoing reactions. Our results show that for some types of graphite anodes, methane participates effectively in the anodic reaction.

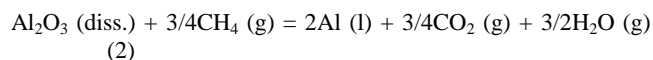
Introduction

In the current industrial aluminium production process (Hall-Héroult process) consumable carbon anodes react with the oxygen-containing ions in the electrolyte at the anode/electrolyte interface. As a result, a large amount of CO₂ as the main gaseous product is emitted. The following reaction can be considered as the overall reaction of the process [1]:



This large amount of generated CO₂ is one of the major weaknesses of aluminium production process; since CO₂ is a greenhouse gas. To solve this problem an inert anode can be used which changes the anodic reaction to oxygen evolution. But a suitable material as an inert anode in the current aluminium electrolysis process must fulfil several requirements. [2]. There have been only laboratory and bench scales tests to try inert anodes so far. In reported one case, Rusal announced their plan to run some industrial scale testes in forthcoming years [3]. In conclusion, a prospective industrial inert anode still seems to be unreachable; at least in the near future.

Another possibility is to supply a reducing gas (*e.g.* CH₄) to the anode/electrolyte interface through a porous anode. Then, the gas participates in the anodic reaction and the overall reaction changes from (1) to the one shown below:



For supplying the gas a porous anode must be used. The porous anode could be made of carbon or an inert material. If it is made

of an inert material, then according to the stoichiometry of reaction (2) the amount of emitted CO₂ can be decreased to half. However, as mentioned earlier a sufficiently inert anode has not been found so far. Therefore, a porous anode made of carbon seems to be a more practical choice at the present time. If the anode is made of carbon, either of the two reactions can occur at the anode. The theoretical cell voltage of reaction (2) is 1.1 V at 1233 K (960°C) while for reaction (1) it is equal to 1.2 V at the same temperature [4]. Therefore, thermodynamically reaction (2) is more favourable; although the difference is small. This difference is due to depolarisation effect of the gas [4, 5]. Besides, utilizing the reducing gas, *e.g.* CH₄, results in reduced CO₂ emission. The degree of CO₂ emission reduction depends on which of these two reactions dominates as the anodic reaction.

The idea of utilizing a reducing gas for the anodic reaction of aluminium electrolysis has been tested before. Injecting of methane to graphite anodes in two series of experiments resulted in lowering the polarization voltage by 0.3-0.4 V [6]. In another study [7], gas electrodes made of graphite (50% porosity) were flushed with methane. But the anode was clogged by soot. When H₂ and CO were used some depolarization was observed; though the carbon consumption increased and the anodes disintegrated. Also anodes made of magnetite were used. They showed higher stability but eventually disintegrated after long time [7]. In a similar study porous graphite anodes showed depolarization when methane and H₂ were used. It was mentioned that due to high temperature of the process, methane decomposition occurs considerably and methane can be considered electrochemically equivalent to hydrogen. Carbon monoxide reacted only in the presence of catalysts and showed much less reactivity. Considerable fluoride losses from electrolyte occurred when hydrogen-containing fuels were used [8]. Lately, a study from New Zealand, have reported use of nickel alloy hydrogen diffusion anodes tested in a potassium-based electrolyte for aluminium production. Although a noticeable depolarization was observed, the metallic anode showed relatively low stability [9]. There are also a few patents in this field. One is a non-consumable gas anode based on the type used for Solid Oxide Fuel Cells (SOFC). Although, this anode is not suitable for the current aluminium electrolysis process, and could be utilized in a modified Hall-Héroult process [10]. The other patent is an anode made of porous graphite or a carbon based material. The anode has the roles of both conducting electricity and conveying and distributing the reducing gas [4].

We have been working on this concept of reducing gas-supplied anodes for aluminium electrolysis using porous anodes; both inert (*e.g.* SnO₂) and graphitic; where methane and H₂ were chosen as reducing gases and a modified electrolyte at 850°C was used [5, 11, 12] Considerable depolarization was detected when using SnO₂ anodes. Flushing methane through graphite anodes also showed a tiny depolarization effect [5]. Due to probable

dissolution of SnO₂ anode in the electrolyte, in the present study we have focused on graphite anodes using an electrolyte similar to what is used in industry for production of aluminium.

Experimental

The electrolyte composition was 6 wt. % AlF₃ (Noralf, Boliden Odda AS) and 5 wt. % CaF₂ (Merck, > 97 %), 4.5 wt. % anhydrous γ -Al₂O₃ (Merck, > 98 %) and remaining Na₃AlF₆ (natural cryolite, Greenland). The cryolite ratio was 2.5 and it was saturated with alumina. Figure 1 illustrates the schematic of the experimental set-up. A graphite crucible contained the electrolyte. The walls of the crucible were lined with alumina and its bottom served as the cathode. A hollow steel tube screwed to the porous carbon anode was used as current collector. The anode and cathode were positioned horizontally in respect to each other. A molybdenum wire (Norsk Spesialmetall, 99.9 pct) wire (1 mm \varnothing) was used as the current collector. The wire was passed through an alumina tube and both were placed into another alumina tube. The outer alumina tube contained aluminium at the bottom. There was a small hole near the bottom of the outer alumina tube where electrolyte could enter the reference electrode. The whole system served as an Al³⁺/Al reference electrode. All of the potentials were measured versus this aluminium reference electrode. The crucible containing the bath was dried in air at 120°C overnight. Furnace and bath were also dried at 200°C in N₂ for a few hours before heating up the furnace to the working temperature at 970°C. The furnace was continuously flushed with N₂. The inlet gas composition for the anode was controlled using mass flow controllers (Bronkhorst) and the inlet gas pressure was measured. The whole electrochemical cell was placed in a vertical tube furnace heated by resistance wires, and connected to a temperature controller. The gases were flushed into the porous anode with the gas flow equal to 20 ml min⁻¹.

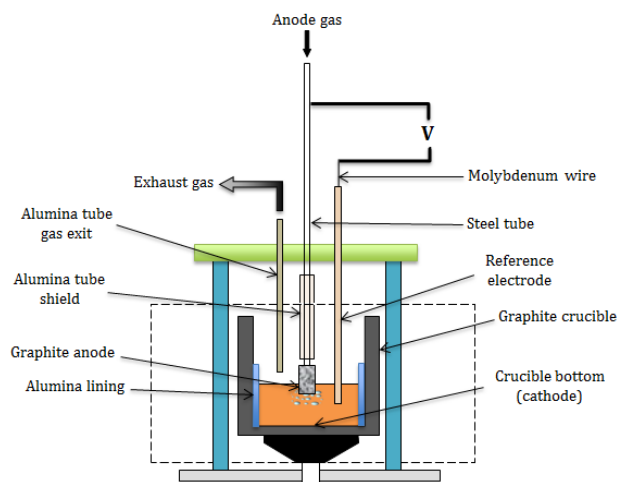


Figure 1: Schematic of the electrolysis cell.

Galvanostatic electrolysis experiments were performed using porous anodes made of three different graphite grades (Tokai Carbon Group). Some of the properties of graphite grades used for preparing anodes are given in Table I. Each experiment was started by applying a constant current of 2.3 A to the cell - corresponding to an apparent current density of 0.4 Acm⁻² - while N₂ was passed through the porous anode for the first 45 min of the electrolysis time and afterwards changing the gas to CH₄ and

continuation of the electrolysis for 4 h (total time: 285 min). This procedure enabled us to detect if there is any depolarization upon introduction of the CH₄ to the anode. Also another series of electrolysis experiments were carried out without using methane for comparison and in order to have a better insight of the process and for comparison. In this series, only nitrogen was flushed into the anode; while the rest of the experimental conditions were unchanged. The weight of the anodes was measured before and after each experiment to check the consumption of the anodes and it was compared with the theoretical values.

The graphite anodes were studied by Scanning Electron Microscope (SEM, Hitachi S-3400 N).

Table I: Typical properties of different graphite grades[13]

Grade name	Specific gravity (g/cm ³)	Porosity (%)	Grain size (μm)	Grade
G347	1.85	12	11	Isotropic
G140	1.7	20	1000	Moulded
KWPSY	1.6	20	2000 ¹	Extruded

¹Maximum grain size

Results and Discussion

Table II summarizes the consumption of the porous graphite anodes in electrolysis experiments. The theoretical consumption based on reaction (1), *i.e.* assuming that CH₄ does not take part in the anodic reaction, is 1.2 g.

As it can be seen, the isotropic graphite (G347) behaved quite differently compared to two other grades. There is a significant change in weight loss of the anode during electrolysis when CH₄ was supplied through G347 compared when N₂ was supplied through the anode. The moulded (G140) and extruded (KWPSY) grades were also consumed slightly less, when CH₄ was flushed into the anode but the difference is less significant compared to G347. It seems when isotropic grade was used, CH₄ participated in the anodic reaction remarkably, while for the two other grades anode consumption is almost equal to the theoretical value. The weight loss difference of the extruded grade anode (KWPSY) with and without CH₄ is not very small. But this is due to the fact that this anode showed a higher consumption when N₂ was used, compared with two others. The reason for this is not clear at the moment.

Generally, the amount of anode consumption is expected to be higher than the theoretical value. In industry the carbon consumption is around 110-120 % of the theoretical value. This is due to the unwanted consumptions of anode such as CO₂ burn (Boudouard reaction) especially when the gas penetrates into the pores of the anode, air-burn, and dusting [1].

However, it is seen here that for all the graphite grades when CH₄ was applied, the weight loss was less than theoretical consumption. Hence, it is likely that CH₄ was involved in the anodic reaction - at least to some extent - for all graphite grades. This conjecture sounds more probable when we consider the probable thermal cracking of CH₄ resulting in precipitation of carbon in the porous structure of the anode. Methane becomes unstable in terms of its elements from 530°C. However, the kinetics is slow. The equilibrium constant for cracking of methane is 87 at T = 970°C [14]. Therefore, this reaction is most likely to happen in our experiments, at least to some extent. Precipitated carbon can add to the final weight of the anodes. One experiment was performed to check this, where all the conditions were unchanged, except that no current was passed. So, the sole factor

influencing the anode weight was the amount of carbon precipitation. It was found that around 0.2 g carbon was precipitated in 4 h (the same time CH₄ was flushed into anodes during electrolysis experiments). Consequently, the amount of graphite consumption was probably even less than the values reported in Table II. This means that methane has been involved in the anodic reaction even more.

Table II: The consumption of graphite anodes when supplied with only N₂ and when supplied with N₂ + CH₄ during electrolysis in cryolite-based electrolyte at 970°C for 285 min. The theoretical consumption is 1.2 g.

Graphite type	Anode gas	Weight loss (g)	Consump. (%)
Isotropic (G347)	N ₂ + CH ₄	0.67	56
	N ₂	1.28	107
Moulded (G140)	N ₂ + CH ₄	1.15	96
	N ₂	1.24	103
Extruded (KWPSY)	N ₂ + CH ₄	1.16	97
	N ₂	1.4	117

Apart from the electrochemical reaction and cracking reaction, there exists another factor which might have changed the anode weights. This is the electrolyte which enters the porous structure of the graphite during electrolysis and can add to the final weight of the anode. However, this seems to be negligible since in all the experiments when the electrolysis was finished the anode was pulled out of the bath and was flushed with N₂ for 1 hour. This caused the remained electrolyte, if some, to be pushed out of the anode. SEM studies of the graphite anodes also confirmed that the graphites structure was almost electrolyte free after the experiments.

Error! Reference source not found., shows the pressure measured before the anode upon introduction of gas (N₂) to the anode for different graphite grades. As can be seen, different graphite grades behaved differently when the gas (N₂) was introduced into the anode. This was before submerging the anode into the salt bath and the anode was placed 2 cm above the melt.

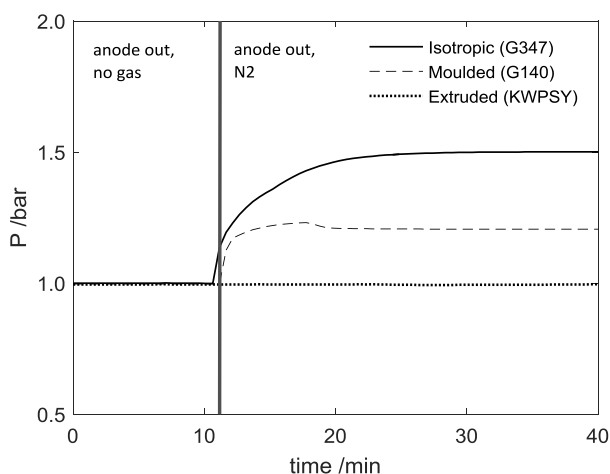


Figure 2: Measured pressure before the anode, upon introduction of gas (N₂) to the graphite anode for different graphite grades; Solid line: Isotropic (G347), dotted line: Moulded (G140) and dashed line: Extruded (KWPSY).

The isotropic grade showed the largest pressure increase, around 0.5 bars, the moulded grade showed less increase, around 0.25 bars; while the extruded grade did not show any pressure increase. This difference can be attributed to the large difference in grain/pore size of these graphite grades. The pores in the extruded grade were large enough to avoid any resistance for the flow of the gas.

Error! Reference source not found. shows the cell potential and pressure changes during aluminium electrolysis using isotropic grade (G347) anode for two different experiments; **Error! Reference source not found.** (a) show only N₂ supplied through the anode and **Error! Reference source not found.** (b) show N₂ was supplied through the anode 45 min prior to introducing CH₄ and the electrolysis was continued for 4 more hours.

As can be seen, when only nitrogen was supplied to the anode, the potential increased gradually during the electrolysis, but the pressure remained constant. This is due to the consumption of graphite resulting in decrease of surface area and consequently increased current density. This is in agreement with previous studies demonstrating an increase in the anodic overvoltage when current density is increased [15].

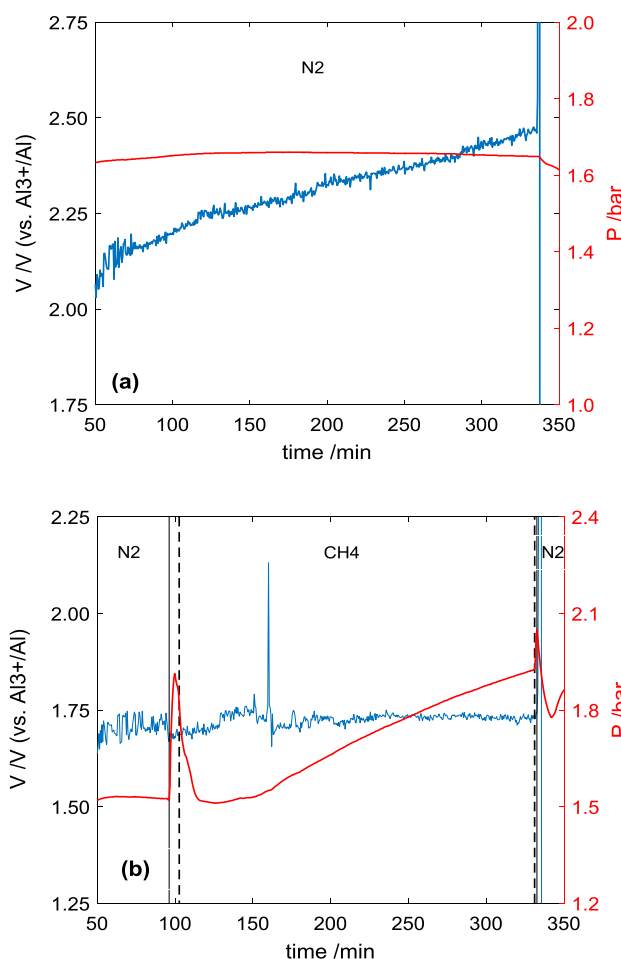


Figure 3: Potential and pressure changes during aluminium electrolysis for two experiments where in (a), only N₂ and in (b) N₂ + CH₄ were flushed into the porous anodes. Anode was made of isotropic graphite (G347). I=0.4 A.cm⁻², T=970°C.

A rough calculation demonstrates that the change in the surface area was noticeable. The surface area prior to electrolysis was 6.28 cm^2 and the approximate value for the final surface area was: $A_f \approx 5 \text{ cm}^2$. The final surface area was calculated based on the geometrical surface of the anode after electrolysis. Assuming the change in surface area and a constant current the apparent current density increased from 0.37 A.cm^{-2} to 0.46 A.cm^{-2} during electrolysis.

However, when CH_4 was introduced to the anode the potential became stable and it remained almost constant throughout the electrolysis period. The vertical lines in Figure 3 (b) represent the time where the gas anode was shifted from nitrogen (dashed line) to methane (solid line). There was an abrupt increase and decrease in pressure which is because of supply of both gases during the shifting time. After that as can be seen, introduction of methane to the anode caused a gradual pressure increase which lasted as long as methane was flushed; *i.e.* until the end of electrolysis. This is due to carbon precipitation from the cracking reaction of methane. If the electrolysis continued for a longer time, this might have led to clogging as observed earlier [7].

The change in cell voltage agrees with the weight loss data (Table II). It is clear that methane was significantly involved in the anodic reaction, so the potential was stable and did not increase. However, the problem of clogging might prevent long term electrolysis. A suitable anode design could possibly prevent the probable and undesirable clogging.

There is a small difference in the cell potential in the beginning between these two experiments, although the anodes were similar and both experiments were started by supplying N_2 to the anode. The reason is not clear.

The potential and pressure changes for the two other graphite grades (G140 and KWPSY) are illustrated in **Error! Reference source not found.**; both when there was only N_2 (a) and when CH_4 was also used as the gas anode, (b) and (c). As can be seen, when N_2 was introduced through the anode the potential showed the gradual increase during electrolysis as also observed for isotropic grade (**Error! Reference source not found.** (a)); which was due to increased current density.

In contrast to the isotropic grade (G347), **Error! Reference source not found.** (b), providing the anode made of the other two graphite grades with methane, did not change the potential behaviour, **Error! Reference source not found.** (b) and (c). The potential behaviours were similar to the experiments where only N_2 was flushed to the anode, **Error! Reference source not found.** (a). So, it suggests that the contribution of the methane in the anodic reaction was not significant in these cases and this is in agreement with results from the weight change results. Moreover, by comparing the cell voltage during electrolysis between the isotropic grade and the two other grades, it is revealed that the potential fluctuations were much less pronounced. The observed fluctuations in cell voltage can be due to bubble formation when introducing the gas through the anode. It is assumed that smaller grain pore size due to smaller grain size will result in smaller bubble sizes which finally will result in weaker fluctuations in the cell voltage.

Pressure changes are also shown for the experiments where CH_4 was used as reducing gas, **Error! Reference source not found.** (b) and (c). It is clear that in case of moulded grade (G140) similar to isotropic grade (G347), carbon precipitation led to pressure build up; although to a lower degree. However, the extruded grade (KWPSY) did not show any pressure build up. This can be attributed to the larger grain/pore size of this grade, as mentioned before. The pressure changes during electrolysis for these grades

are consistent with those observed upon introduction of gas to the anode, **Error! Reference source not found.** In the experiments were only N_2 was used no pressure build-up was observed; since there was no carbon precipitation from gas.

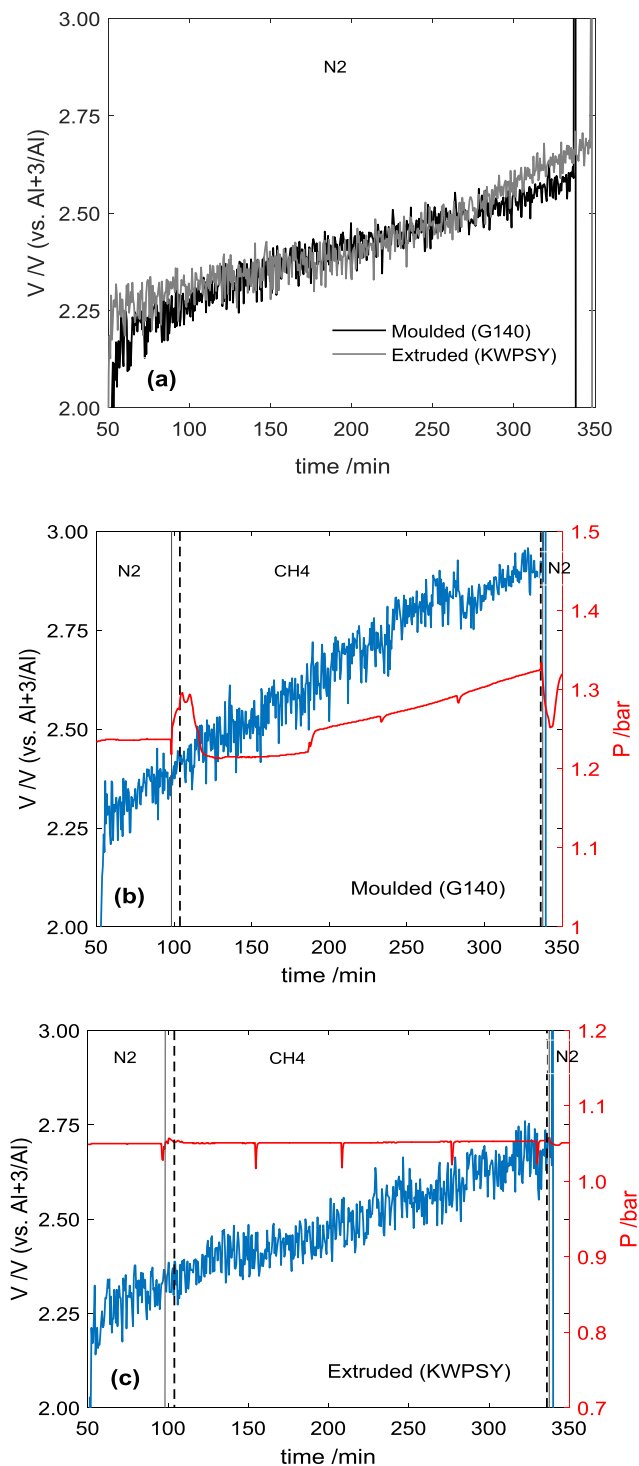


Figure 4: Potential and pressure changes during aluminium electrolysis where only N_2 (a), or $\text{N}_2 + \text{CH}_4$ were flushed into the porous anodes made of moulded (b), and extruded (c) graphite grades. $I=0.4 \text{ A.cm}^{-2}$, $T=970^\circ\text{C}$.

Figure 5 shows micrographs of fracture surfaces of the extruded (KWPSY) and isotropic (G347) graphite grades after electrolysis in cryolite-based electrolyte for 285 min at 970°C; $i = 2.3$ A.. For the extruded grade Figure 5 (a) and (b) it is clear that there was

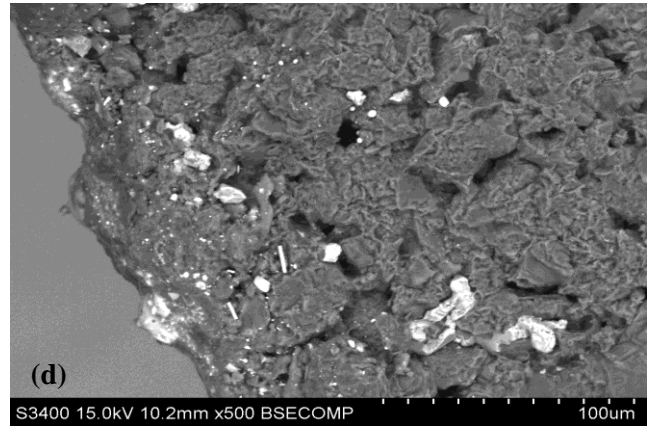
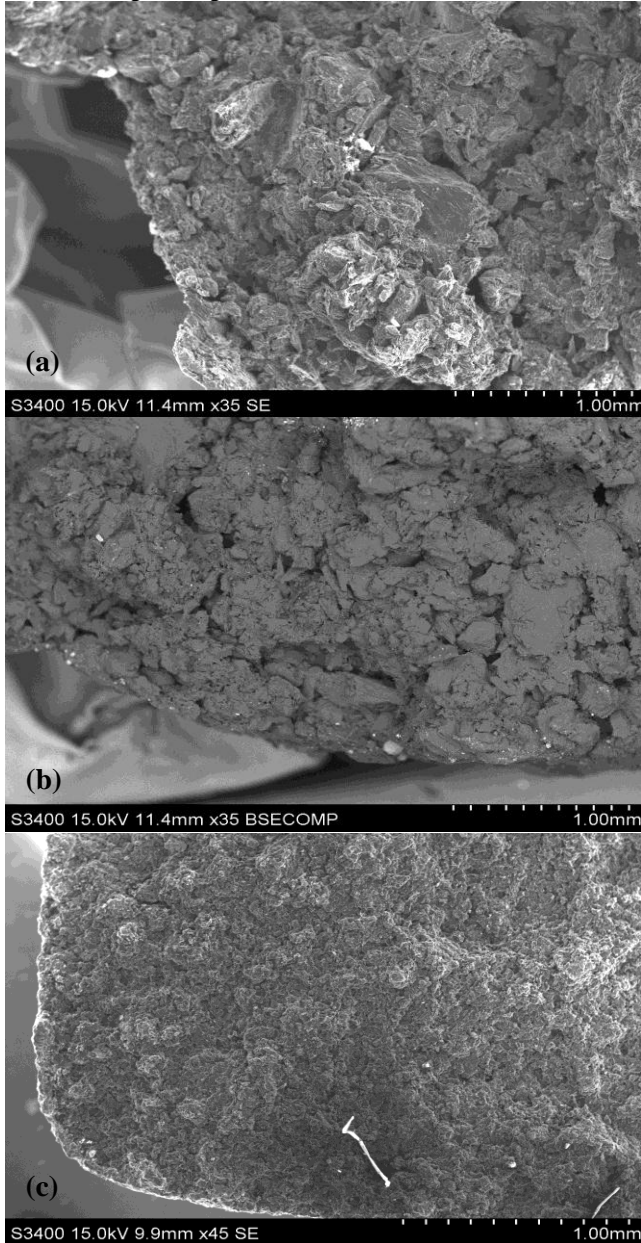


Figure 5: SEM images of porous anodes. (a) SE and (b) BS image (extruded grade). (c) SE image, (d) BS image (isotropic grade).

no electrolyte left inside as little elemental contrast is observed in the back scattered electron micrograph after electrolysis and consecutive N_2 flushing.

This grade is quite coarse as can be seen in the images. Figure 5 (c) and (d) show fracture surface areas from and isotropic (G347) graphite grade.

This grade is much finer. There are small amounts of electrolyte left inside the structure very close to outer surface.

Chemical analysis confirmed that the second phase is electrolyte. This might be due to smaller size of pores and finer structure of graphite which hinders the exit of electrolyte from the anode. Nevertheless, this amount seems to be negligible regarding the weight change of the anode.

Conclusion

In conclusion, the isotropic graphite grade (G347) showed a better performance as a gas anode compared to the moulded and extruded grades. From the weight change results and potential behaviour it is clear that methane participates in the anodic reaction in a large extent when isotropic grade was used compared to the two other grades of graphite. The fact that isotropic grade behaved differently from the two others is mainly due to the much finer structure. It seems the finer grain/pore of the isotropic grade provided a better gas distribution and the three-phase boundary was well established. Further studies including off-gas analysis which can confirm our findings is undergoing.

Acknowledgment

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