ELECTROCHEMICAL CHARACTERIZATION OF CARBON ANODE PERFORMANCE

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Abstract

Coke used in the manufacturing of anodes is commonly a mix of cokes from several suppliers to meet the customer's specifications. This variation in coke composition from suppliers may lead to considerable deviation in anode performance. The present work, still in its early phase, aims to develop a method with which to characterize electrochemical performance of anodes and relate this to the anode material properties. To verify the experimental approach, laboratory anodes were produced from various single cokes with different impurity levels. Voltammetry was performed and polarization curves were recorded to investigate current-voltage characteristics of these anodes. Gas analysis was also executed in order to study the CO_2:CO ratio and calculate Pearson-Waddington current efficiencies. The reaction overpotential from polarization curves was found to decrease with increasing total metallic and sulphur impurities, indicating that blended cokes may behave differently on a microscopic scale and between individual anodes in a cell if the anodes come from different production batches. Contrary to the polarization curves, metallic and sulphur impurities were found to not significantly change the CO_2:CO ratio or Pearson Waddington current efficiency. Experiments of this type aim to develop fundamental understanding of how single coke properties affect electrochemical performance.

Introduction

Anodes are traditionally made by using a blend of various single source cokes [1, 2]. However, although the blends from the coke supplier are within certain analytical specifications, anode quality can still vary widely [3]. Reasons for this are not fully understood and more fundamental studies are required.

Many papers have therefore studied how changes in coke properties, such as structure and density, affect anode performance [4-6]. The effects of coke impurities on anode performance have additionally been widely studied: iron, vanadium, calcium and sodium are found to enhance the combustion of carbon in air and its reaction with CO_2 [4, 7-9]. Studies indicate these impurities can also affect the anodic reaction, causing increased electrolytic anode consumption and/or decreased overpotential [8, 10-13]. Sulphur acts as an inhibitor of these catalysts possibly due to metal-sulphide formation [8], and has therefore been shown to retard CO_2 and air reactivity of anodes [9]. It has additionally been associated with lowering current efficiency (CE) [14] and varying degrees of anode dusting [8, 14]. Most researchers have investigated this field of 'electrocatalysis' by artificially distributing dopants (metals, metal oxides and salts) throughout a coke before production into green anodes. However, artificially added dopants are probably not fully incorporated into the coke bulk structure. Fewer publications (such as [15]) have studied the natural variation of impurities in single cokes and their effect on electrochemical performance.

Anodes made from single cokes may give a better elementary understanding of the coke properties with the most pronounced effect on the overall anode performance. This study attempts to develop a method with which to distinguish the electrochemical performance of anodes made from different single cokes, and correlate this to anode properties such as impurities. The method is based on determining reaction overpotential; an important factor approximating to the energy required for the anodic reaction to occur. Although difficult to separate out from the measured anodic potential, the anodic reaction overpotential should be the only variable between experiments (as detailed in Figure 1) when comparing potentials at the same current density (CD). This means comparative values of reaction overpotential between a series of materials can be given. Voltammetry and gas analysis are also used to support and explain the electrochemical results, and provide a measure of the CE using the Pearson-Waddington (P-W) Equation [16].

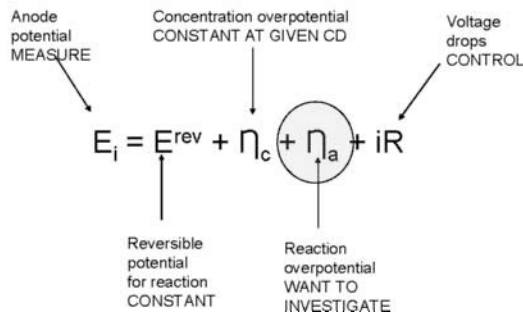$$CE(\%) = 100\% - 0.5\ [\%CO_{(g)}] = 50\% + 0.5\ [\%CO_{2(g)}] \qquad [1]$$

Figure 1) The measured potential (E_i) is composed of numerous terms, including the reversible potential (E^{rev}), concentration overpotential (η_c), reaction overpotential (η_a) and voltage drop (iR)

Materials and Method

Experiments were performed in a cryolite melt (cryolite ratio = 2.3 (cryolite from Sigma Aldrich, purity >97%), excess AlF_3 = 9.8 wt% (industrial grade AlF_3 sublimed in-house), alumina concentration = 9.4 wt %, (γ alumina from Merck). The melt was contained in a graphite crucible (Svensk Specialgrafit AB, Sweden), in which alumina crucible shields and a copper-plate cathode were inserted (schematics in Figure 2). An aluminium reference electrode in an alumina assembly was fabricated according to [17]. Four types of single cokes were used to produce pilot scale anodes using fraction size 2-0 mm. The production of the anodes varied only in the coke type, all other parameters were kept constant. Anodes were labeled 1-4, core drilled into cylindrical rods with dimensions 60 x 10 mm, and screwed into stainless steel rods. Parallels of anodes types 1-4 were additionally analyzed using XRF to determine the impurity content (including sulphur and total metallic elements).
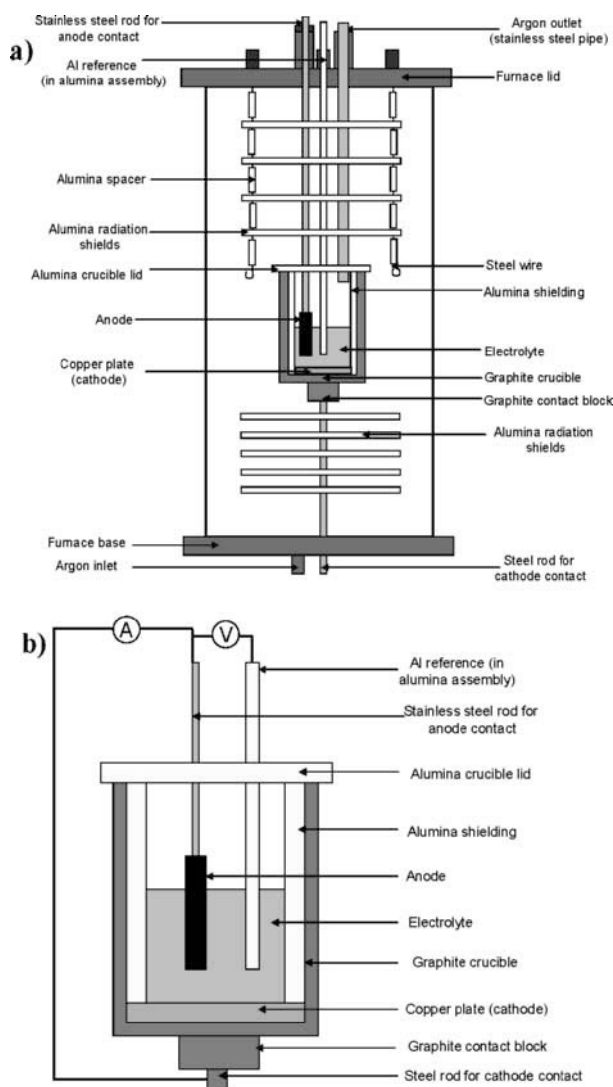

Figure 2a) The location of the crucible inside the furnace tube, and Figure 2b) A close up of the crucible and its contents (gas outlet removed for simplicity), detailing how potential is applied to the anode and current measured

Each anode was lowered into the melt to a depth of 1.5 cm (although accurate immersed areas were measured after experiments), giving an approximate active electrode area of 5.5 cm^2. Electrochemical Impedance Spectroscopy (EIS) was used to determine the ohmic resistance at the Open Circuit Potential (OCP), the value of which was used to iR compensate all electrochemical measurements during experiments. Although the additional resistance with current flow (for example, bubble resistance) was not compensated, this would be approximately the same for each material at any given CD. Linear sweep voltammograms were produced at 1 V s^{-1} before one polarization curve was recorded for each anode by slowly sweeping the anode potential (relative to the aluminium reference electrode) from the OCP to 2.6 V at 2 mV s^{-1}, and measuring the responding current. All electrochemistry was performed using an Autolab PGSTAT 20 (with built in Frequency Response Analyzer (FRA) and 10 A booster, all from Eco Chemie)

To relate the polarization curves/voltammetry to reaction products, mass spectrometry (MS, ProteaProMass) was used in combination with gas chromatography (GC, Agilent μGC series 3000) to measure CO and CO_2 content in the gas outlet, based on an adapted method from Kjos *et al* [17]. GC and MS techniques had different sampling rates and varying degrees of accuracy; MS has a low sampling time and volume but drift due to vacuum renders data less quantifiable. GC produces quantifiable data, although collection is slow due to elution times of four minutes. Thus, to determine concentrations, the slow throughput (but accurate) GC data was used to continuously calibrate the high throughput (less accurate) MS data.

The order of the anode materials tested was randomized to eliminate possible changing characteristics of the melt over time, and two parallels were performed for each material (with new anodes) in the same bath. Bath samples after each anode experiment were taken for subsequent oxide content analysis (LECO analyzer model TC-436DR).

Results and Discussion

Electrochemical measurements

The measured polarization curves showed a steep increase in current relating to the main anodic reaction during aluminium electrolysis where CO_2 (and possibly some CO) is formed (see Figure 3 for a typical polarization curve). Due to the relatively large reaction overpotential involved, the potential where a large increase in current occurred was approximately 300 mV higher than the standard potential for CO_2 formation. No diffusion limitations were observed in the potential range studied, probably due to the fact that the melt was saturated with alumina. The produced polarization curves were used to get a comparative value of the reaction overpotential of each anode type (containing different cokes). LECO measurements of all the melt samples showed little variation in alumina concentration over the course of the experiments, meaning all potential differences could be considered due to the materials only. Owing to the fact that all anodes had identical distribution of grain size and pitch type/level, these variations in potential must relate to differences in the coke properties such as impurity levels.

The CD chosen for comparison was 1 A cm^{-2}, as this is close to industrial conditions. Comparison of the potential at 1 A cm^{-2} in Table 1 showed a standard deviation (STDEV) of 0-50 mV for repeats of the same material, with reaction overpotentials between different materials varying by 40-200 mV. As the experimental STDEV was lower than the average material differences, resolution of reaction overpotential trends could be observed between the anodes. The order of reaction overpotential of the materials (high to low) correlated with increasing levels of total metallic impurities and sulphur. As metallic impurities can catalyze air and CO_2 reactivity, it would also be expected these can additionally catalyze the anode reaction and reduce anode overpotential [10]. This trend correlates with previous studies which showed that metallic dopants such as vanadium, calcium, sodium and iron could lower anodic overpotential and increase electrolytic anode consumption [8, 12, 13]. Although the order of overpotential also correlated with increasing sulphur, a known catalyst inhibitor [8, 9], it is possible that the sulphur in the anodes requires time to accumulate at the surface to act as reaction inhibitor. Additionally, some studies showing sulphur as a catalyst inhibitor used artificially doped sulphur, with most sulphur residing in the binder coke – a different situation than with naturally occurring coke sulphur [8]. However, due to the fact that many other properties vary between coke types, further important factors towards overpotential could include surface morphology (porosity) and structural composition of the coke; both not discussed in this paper.
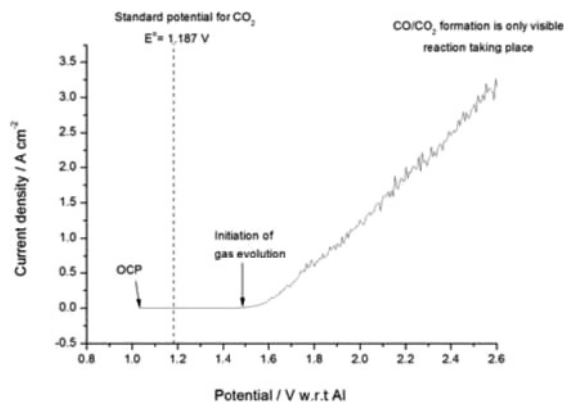

Figure 3) A typical polarization curve showing a scan from OCP to 2.6 V w.r.t Al. Detailed are the standard potential for CO_2 formation and the initiation of gas evolution.

Table 1) Average anode potential and STDEV/ V w.r.t Al (at 1 A cm^{-2}) and anode impurities.

Material	Average potential / V	Order of anodic overpotential (high to low)	Content of impurities (low to high)	
			S	Total metallic impurities
Anode 1	1.94 ± 0.00			
Anode 2	1.90 ± 0.03			
Anode 3	1.84 ± 0.00			
Anode 4	1.74 ± 0.05			

Similar to the polarization curves, the main feature on the linear sweep voltammograms was the large increase in current relating to the main anodic reaction of CO_2/CO formation (Figure 4). Additionally, there was a smaller peak at lower potentials which, although difficult to identify, has previously been related to adsorption [18]. Since the electrolyte was saturated with alumina, the sweep rate dependency of the current response was very limited. With no mass transport limitation, the system showed kinetic control. There were therefore similar correlations between the reaction overpotential/CD and the anode types as found from analyzing the polarization curves. For example anode 1 (with lowest metallic and sulphur impurities) had the lowest CD from voltammetry and highest reaction overpotential from polarization curves, whilst anode 4 (with highest sulphur and metallic impurities) had the highest CD and lowest reaction overpotential.
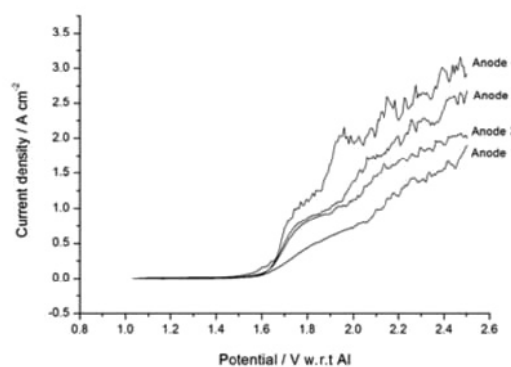

Figure 4) Linear sweep voltammetry curves of the anode materials tested, showing variations in CD.

Gas analysis

Gas analysis showed that the main anodic product was CO_2, but substantial amounts of CO was also detected. CO arises mostly from the back reaction, but could also have been formed electrochemically or via the Boudouard reaction. As expected, the concentration of CO and CO_2 started to increase exactly where the current started to rise rapidly (Figure 5). The CO_2:CO ratio and P-W CE were found to increase with potential (Figure 6), possibly due to a decrease in the retention time of the produced CO_2 in the melt, leading to a decrease in back reaction.
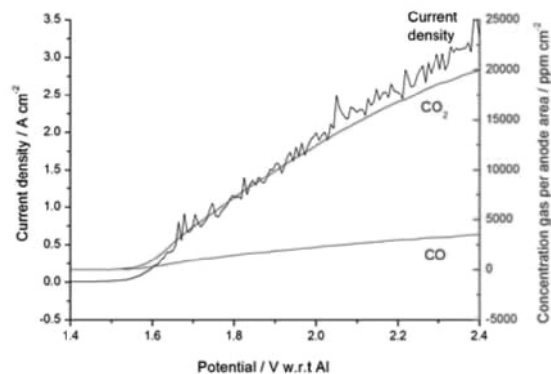

Figure 5) A typical polarization curve with measured CO and CO_2 concentrations over the potential range studied.
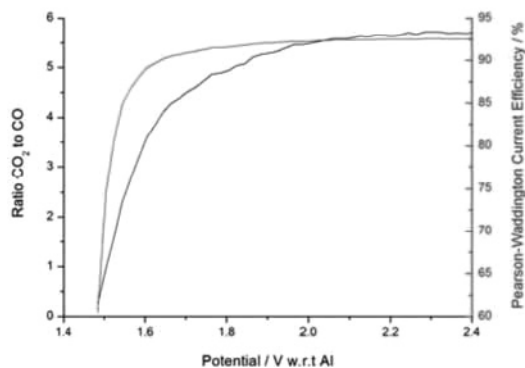
Figure 6) Typical $CO_2:CO$ ratios and P-W CE over the potential range studied.

Generally, all materials produced similar amounts of CO_2 and CO at 1 A cm^{-2}, giving similar P-W current efficiencies. The concentration of CO_2 was usually around 6000 ppm (at 1 A cm^{-2} and constant carrier gas flow), with a theoretical value of 9000 ppm. Using the P-W Equation and assuming all CO is produced from the back reaction, the CE was calculated as ~ 90% for the materials (Table 2). In contrast, previous studies have indicated that high levels of metallic impurities such as vanadium lower the CE, possibly due to the presence of multivalent oxides and higher non-electrolytic anode consumption [15]. The fact that CE did not correlate with metal impurities in the current study could be due to the scale of the experiments, i.e., laboratory vs. industrial. Interestingly, anode 1 (with the lowest sulphur content) produced gases with a smaller $CO_2:CO$ ratio than the other anodes tested. Previous studies have found increasing sulphur increases dusting [8]; others found that levels of Boudouard reaction, dusting, and current efficiency do not change significantly within a range of 2-3.8% anode sulphur content [14]. Discrepancies are not easy to explain, but indicate a complex influence of impurities on the anode process, difficult to comment on at this stage.

Table 2) A summary of the gas ratio and P-W CE for each anode type (at 1 A cm^{-2}) and STDEV

Material	Average ratio $CO_2:CO$	Average P-W CE / %
Anode 1	3.0 ± 0.3	87.6 ± 0.9
Anode 2	4.1 ± 0.0	90.3 ± 0.0
Anode 3	4.3 ± 0.0	90.6 ± 0.0
Anode 4	4.4 ± 0.2	90.5 ± 0.6

Conclusions

In contrast to studies where dopants are artificially added to raw cokes or cokes are blended to achieve differing impurity levels, this study investigated four anodes containing a single coke type (all other parameters constant). An electrochemical method was then used successfully to obtain comparative measurements of the reaction overpotential of each anode, which were related to anode impurities. Results indicated that the anodic reaction overpotential varied by 200 mV between the materials tested, and decreased with increasing total metallic impurities and sulphur levels. Whilst metallic impurities are known to exhibit electrocatalytic behaviour, sulphur is a known catalyst inhibitor.

Generally, all anodes produced similar gas ratios and PW C-E, although the anode with the lowest sulphur content produced a lower $CO_2:CO$ ratio than the others.

Understanding the relationship between single coke properties, physical anode properties and electrochemical characteristics (such as overpotential) is crucial to avoid issues resulting from blending. Future work in this project will continue to strive to develop a better fundamental understanding of how coke properties affect the anode performance.

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