Evaluation of Gas Composition from Laboratory Scale Electrolysis Experiments with Anodes of Different Sulphur Content

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Abstract

With the anticipated decrease in available anode raw materials, future anodes are expected to contain higher levels of impurities. Currently the implications of this are being investigated through evaluation of electrochemical performance of anodes and the environmental aspects through gas evolution studies. In this work, four experiments of aluminum smelting have been conducted with anodes of varying sulphur content. The aim of this work was to evaluate the speciation of sulphur in the off-gas. It was found that COS is the main sulphur species in the inert argon furnace atmosphere. The gas composition was further evaluated as a function of set anode voltages in potentiostatic mode. The significance levels of gas composition were evaluated through repeated experiments. As an FTIR multicomponent analyzer was used, less commonly discussed gaseous constituents such as CH_4 and HCl were evaluated with respect to given impurity levels in the anode.

Introduction

With a decrease in the availability of high quality materials for anode production, the anodes produced will show decreasing performance in the physical parameters used as metrics for quality [1]. It is further expected that impurity elements and distribution will be negatively affected. In addition to the physical testing, more recent studies have put emphasis on the electrochemical performance of the anodes, trying to correlate the anodic overpotential with anode composition [2]. Another work by the same author gave evidence of a correlation between anode impurities and anode overvoltage [3].

In future laboratory studies of the electrochemical performance of anodes, a coupling between electrochemical characterization and chemical composition of produced gases has been proposes. In these experiments the sulphur content of the anode has been targeted as an important parameter. The significance level of the sulphur content of the anode has been much discussed: how much change in Sulphur content is required in order to quantify a significant change is sulphur content in the gas phase?

In previous work [4], the potential impact of anode sulphur content on the formation of Perfluorocarbon (PFC) gases was evaluated. In this work, some of these experiments described in [4] have been evaluated for the production of sulphurous gas species rather than the PFC gases. For the high concentrations of CO and CO_2, new gas calibration models were established in order to calculate the sulphur to carbon ratios of the produced gas. Qualitatively, the FTIR spectra were used to evaluate multiple gas species produced, excluding the homonuclear species not providing absorption in the mid-IR range.

Experimental

Laboratory experiments were conducted in an electrolysis setup optimized for anode gas sampling. The anodes were cylindrical with a hollow center. The anode sides were shielded with silicon nitride, extending 0.5 cm below the anode surface. The produced anode gases were fed into the center of the anode by the silicon nitride shielding and a slightly sloping anode surface, and then led out of the furnace through a hollow anode rod. In this way it was possible to recover all produced anode gases with good dynamics. Anode surface area was estimated to be 25 cm^2. A hollow boron nitride rod containing a drop of aluminium metal was used as reference electrode. This setup has previously been described in [4]. The electrolyte used in the laboratory cell was 80% Na_3AlF_6, 12% AlF_3, 5% CaF_2, and 3% Al_2O_3 and the furnace temperature was kept at 960 °C. The anode to cathode distances was kept between 35 and 40 mm.

The experiments conducted are summarized in Table 1.

Table 1. Experimental parameters. S is the baked sulphur content of the anode, Dil is the FTIR dilution flow and ACD the anode to cathode distance.

EXP	Anode	S (%)	Ar (nlpm)	Dil (nlpm)	ACD (mm)
1	A	1.79	0.4		40
2	B	3.29	0.4	0.4	40
3	A	1.79	0.4		35
4	B	3.29	0.4	0.7	35

Due to the high concentration of carbon oxide in the off-gases, various levels of dilution were attempted. The purpose of the dilution was to avoid saturation of carbon oxides while being able to quantify the less abundant gas species.

All experiment were conducted with an inert flow of 0.4 nlpm Ar. Two experiments were conducted with additional dilution of the off-gas as noted above.

The experiments were conducted potentiostatically at varying voltage levels between 3.0 and 4.5 volts. At the end of the experiments, anode effects were induced either amperometrically (EX 1-3) or potentiostatically (EX 4), with the purpose of evaluating any possible difference in off gas composition during the anode effect with respect to sulphur content.
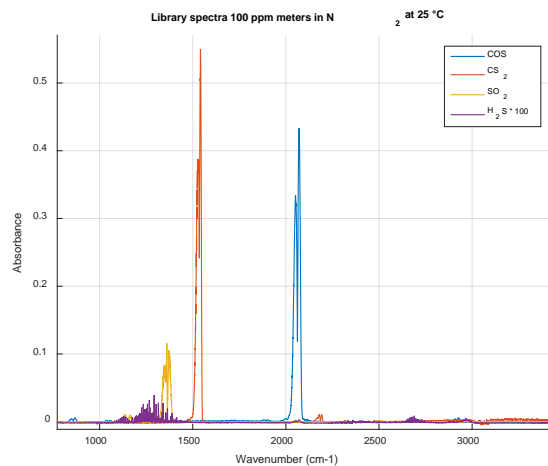
Since the different experiments were conducted with different voltagecurrent profiles and for varying durations, their off-gas concentration versus time plots were not directly comparable. The total concentration of gas constituents produced was estimated by integrating the area under the concentration time curves. For comparison, the current-time curves were integrated and the

charge passed throughout the experiment duration used to estimate total carbon dioxide production under the assumptions of 100 % current efficiency and no losses to Boudouard and/or back reactions.

The gas characterization was conducted with a Protea ProtIR 204M FTIR analyzer. This instrument had a 6.4 meter optical cell and an interferometer resolution of 1 cm^{-1} was applied. The sample line as well as the gas cell was heated to 180 °C. For quantification of gas species, partial least square regression models were built from actual gas constituent spectra. The models were validated for the concentration ranges observed for the experiments conducted.

Results

Interestingly, the only sulphur species found in these experiments were carbonyl sulphide. In order to unequivocally prove the absence of other sulphurous species with the applied gas characterization setup, the calibration spectra of relevant gas species is illustrated in Figure 1. From [5] it was expected to find CS_2 in the samples. Figure 1 shows that the specific absorbance is higher than that of carbonyl sulphide, thus its presence would have been detected if present at comparable concentrations to those of COS. As for sulphur dioxide, this species has lower specific absorbance yet high enough for detection at concentration levels comparable with COS. Sulphur dioxide is however considered a sticky gas and losses to surfaces in the gas extraction channel and analyzer could occur. Sulphur dioxide is considered to be a product of the oxidation of carbonyl sulphide by oxygen gas presence. Hydrogen sulphide has very low specific absorbance thus implying a high quantification level (per cent levels required for detection). The formation of hydrogen sulphide does however require the presence of hydrogen. Even with this criterion fulfilled, its formation would compete with that of methane, hydrochloric and hydrofluoric acids.
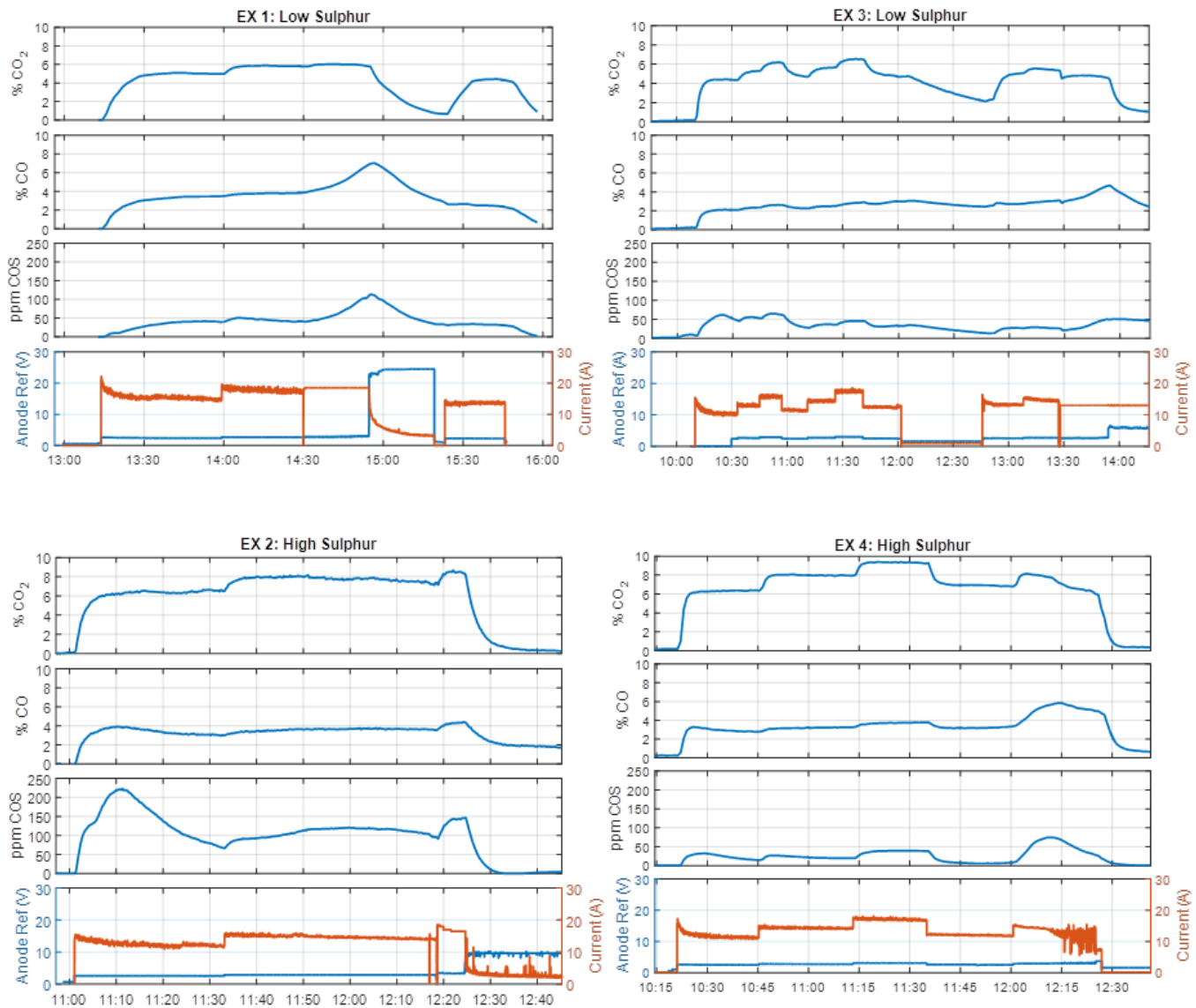
The methane concentration in the off gas was quantified for all experiments. In EX 3 the anode was immersed in the bath for approximately ten minutes before being polarized. As seen from Figure 2, the methane concentration is at its highest when the gas analysis is started upon the anode polarization. This could indicate a non-electrochemical reaction mechanism, which generates up CH_4 at or around the anode, which is then carried out with the electrochemically produced anode gases. For EX 4 it was also found that methane concentration peaked early in the experiment.

As the chlorine content of anode A and B was measured to be 18 and 22 ppm respectively, the hydrochloric acid concentration in the off gas was estimated in order to evaluate the intra-experiment correlation. From Figure 2 it can be seen that the hydrochloric acid concentration profile varies between the experiments. The water content of the anodes has not been determined, but assuming water content between 0.1 and 1 % hydrogen is probably the limiting reagent in the production of hydrofluoric acid, hydrochloric acid and methane. The difference in concentrations for these species is likely due to inhomogeneities in water content of the four 54 mm samples taken from the two anode blocks.
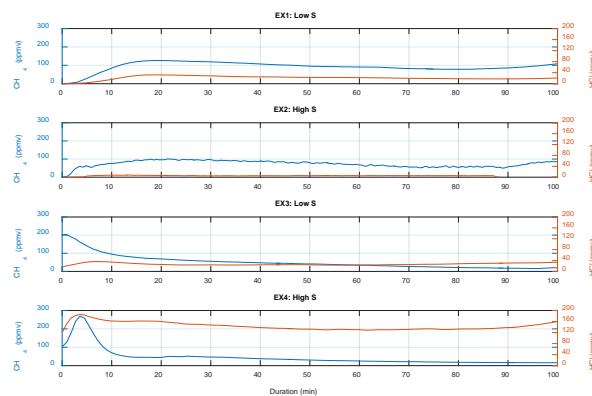
Figure 2. CH$_4$ and HCl concentration profiles.

For the four experiments conducted, the main gas constituents for carbon and sulphur inventories are carbon monoxide, carbon dioxide and carbonyl sulphide. The concentration profiles for these experiments are plotted along with the current and voltage profiles for the experiments in Figure 3.

Figure 1. Calibration spectra of relevant gas constituents at 100 ppm meters in N$_2$ at 25 °C. The H$_2$S signal is 100 fold amplified for illustrative purposes.

Figure 3. Gas concentration profiles for relevant gas species for the carbon and sulphur inventories. The curves are corrected for the dilution factor given in Table 1.

From the current-voltage curves it can be observed that the current varies significantly between the experiments. This is illustrated in Table 2 where the current and voltage data V is summarized for potentiostatic control at 3.7.

Table 2. Current-voltage characteristics and max. CO_2 concentration at 3.7 V setpoint. Average voltage and current values for the interval operated at 3.7 V given.

EX	Vcell (V)	Vref (V)	CO_2 (%)	Current (A)
1	3.58	2.70	5.9	18.5 A
2	3.57	2.91	8.2	14.6 A
3	3.61	2.67	5.3	13.0 A
4	3.70	2.75	8.1	14.5 A

From Table 2 it is clearly seen that CO_2 production and resulting current varies greatly between the experiments. The large

difference in current could not be explained by the 5 mm difference in anode to cathode distance (ACD). The measured difference in ACD (5 mm) was estimated to result in ~ 0.8 A current difference [7] for the experimental conditions in this study.

With the different current voltage applied in the experiment, the total carbon oxide production was compared to a theoretical CO_2 production from the charge passed and assuming 100 % current efficiency and no contribution from Boudouard and back reactions with metal. Total gas production for each experiment was calculated from the initial part of the experiment that was not observably impacted by the anode effect.

Table 3. Gas production ratios. X indicates molar ratio and t theoretical CO_2 production from current passed.

| EX	S / C M	X COS	X CO	CO_2 / tCO2	$CO+CO_2$/ tCO2
1	0.0012	0.00045	0.40	0.42	0.70
2	0.0030	0.0011	0.33	0.64	0.95
3	0.0015	0.00058	0.32	0.50	0.73
4	0.00054	0.00020	0.30	0.72	1.02

As can be seen from Table 3, the mass ratio of sulphur to carbon does not reflect the content of the anode: the experiments with

high sulphur anodes, EX 2 and EX 4, represent both the highest and the lowest mass ratios. The molar ratio of CO is, with the exception of EX 1 fairly stable. The result for EX 1 is consistent with the low CO_2 production at high current seen in Table 2. The ratio of produced CO_2 to theoretical CO_2 production varies greatly due to the difference in current passed. When calculating ratio of the sum of CO and CO_2 to theoretical CO_2 production, an interesting pattern emerges: the yield in CO and CO_2 produced from current passed is significantly higher for the experiments with high sulphur content. In these experiments, the CO and CO2 yield is very close to the theoretical values.

An interesting feature of the carbonyl sulphide concentration profiles found in all experiments is a marked increase in concentration toward anode effect. This is clearly seen in Figure 4. The same effect is also observed in CO. As the electrochemical formation potential of COS is close to that of CO it can be assumed that the depletion of oxide will have the same impact on COS formation as for CO:

$$Al_2O_3 + C + 3S = 3COS + 2Al \qquad E° = \text{-1.04 [6]}$$

In the 3.7 V regime, the COS concentration increases to a level that is not sustained whereas CF_4 increases monotonically. This can also be seen in the other experiments for COS and CO in Figure 3. The change from 3.7 V to 18 A setpoint at 14:30 raises the voltage slightly and both COS and CF4 rises monotonically until gas concentrations peak at 14:54. In this period, the anode reference voltage increased from 2.8 to 3.1 V. Half a minute later the voltage reaches its maximum at 22 V.
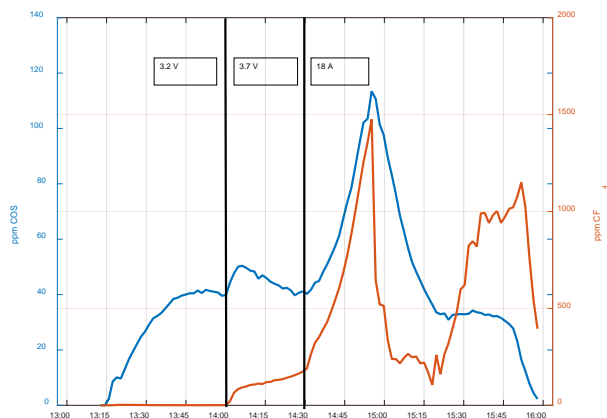
Figure 4. EX 1 COS and CF₄ concentration profiles.

It is likely that during normal electrolysis, enrichment in carbon over sulphur occurs near the anode surface. When exceeding the critical current density of the anode, CO and COS producing reactions become more favorable and the excess sulphur near the anode is consumed.

The correlation between COS and CF_4 is interesting, and it may be speculated that with new quantum cascade lasers [8] available for the mid-IR region, an installation of a gas sensor on the cell duct could function as an early warning sensor for anode effect. How early it would detect the CF_4 onset would depend on the degradation rate of COS to SO2 and also the sensitivity of the laser: the COS increase would have to be discernible from the produced COS from anodes not generating CF_4.

Conclusions

From the current-voltage characteristics of the experiments, it is apparent that the experiments are not amenable to inter-comparison. The variance in current passed is not well understood. Some contribution from Bouduoard and back reactions are expected, but their contributions are not expected to account for the large difference in current. Calculations indicate that the difference in ACD cannot explain the large difference in current. It is possible that shorting through the crucible could vary between the experiments. Measurement of the produced metal could have contributed to the understanding of this problem, however they were not conducted.

The quantitation models built for these experiments appear to be robust. At all dilution levels the models seem to perform well, evaluating from calculation of the residuals. By looking at the gas concentration levels in the various experiments there is no evidence of systematic error in the form of incorrect gas dilution estimations.

The gas composition cannot be corrlated with the sulphur content of the anodes. The sulphur-to-carbon ratios should not be much affected by the currents passed, yet the high sulphur experiments both give the highest and the lowest sulphur to carbon ratios of gas-phase species.

From the concentration profiles of the hydrogenated species, it is concluded that the water content of the samples must vary significantly. It may be speculated that the homogeneity of the sulphur distribution in the 54 mm anode samples is insufficient for the assumption of 1.8 and 3.3 % sulphur in the consumed part of the anode during the experiment. Advanced characterization of anode samples could probably quantify the homogeneity [1].

Further experiments are required in order to gain better experimental control of current-voltage characteristics. Applying identical current-voltage profiles will simplify data inter-comparison of experiments.

Acknowledgement

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