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Electrode specific information from voltammetric monitoring of biogas production

Robert B. Bjorklund[a,*], Anneli Christiansson[b,1], Anders E.W. Ek[b], Jörgen Ejlertsson[b,1]

[a] *Department of Physics, Chemistry and Biology, Linköping University, SE-581 83 Linköping, Sweden*
[b] *Tekniska Verken in Linköping AB, Box 1500, SE-581 15 Linköping, Sweden*

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ABSTRACT

A sensor employing pulse voltammetry monitored the liquid phase of a biogas reactor during 32 days of gas production. An electrode array consisting of stainless steel, platinum and rhodium electrodes generated current responses for a sequence of voltage pulses. Plots of individual current responses against time indicated the electrochemical changes occurring in the broth from the perspective of each electrode. The responses from stainless steel had a pronounced diurnal oscillation which followed the daily introduction and consumption of substrate. The current responses for platinum were in a narrow range whereas those for rhodium exhibited several minima. A disturbance in the reactor caused by omission of substrate led to decreases in both gas production and current responses for all the electrodes. Multivariate data evaluation of all the current responses by principal component analysis indicated the daily fluctuations for concentrations of ions and redox active compounds in the broth.

1. Introduction

Biogas production by anaerobic digestion of organic feedstocks has become an important process for reducing the volume of municipal and agricultural waste and supplying carbon neutral fuel for energy generation. The process is complex, subject to the activity and inhibition of several microbial groups [1]. Digestion is started by hydrolysation and fermentation of biopolymers to hydrogen, carbon dioxide and volatile fatty acids. The latter are oxidised by acetogenic bacteria to acetate, hydrogen and carbon dioxide. These intermediates are finally converted by methanogens to methane, carbon dioxide and water.

Since the bacteria groups involved have differing growth rates and tolerance to environmental changes it is important to avoid disturbances in the balance between the participants. This requirement manifests itself in the need for careful reactor design and the choice of mixing conditions and presence of active microbial biomass. Crucial process parameters for optimisation are organic load rate, hydraulic retention time, temperature, pH, buffering capacity and fatty acid concentrations [2]. Monitoring of load rate, retention time, degree of degradation and methane yield has been reported for large-scale operation [3]. Instability among the intermediate products can lead to accumulation of hydrogen, volatile fatty acids and alcohols leading to fluctuations in gas production and possibly reactor failure.

The relative small scale and decentralisation of biogas production facilities has kept implementation of instrumentation for process control at a low level [4]. Uncertainties during operation often lead to production at less than optimal conditions in order to avoid critical loading and reactor failure. To improve process efficiency, larger facilities staffed with full-time operators are being equipped with in/on/at-line instrumentation to continuously monitor process parameters in the liquid and gaseous phases [5,6]. A number of in/on-line methods are used to monitor the broth for temperature, pH, redox potential (ORP), total organic solids, chemical oxygen demand (COD), acid capacity (as mg/l $CaCO_3$) [7] and total volatile fatty acids [7]. These can be complemented with at-line methods, such as rapid photometric tests, to determine specific chemical species such as ammonium ion which is in equilibrium with the bacteria toxin ammonia [5]. In addition, the identification of individual organic acids by techniques such as ion chromatography [8] has value even with the time delays associated with off-line analysis since particular species such as propionate has been shown to be an early warning marker for process disturbances [9,10].

New analytical methods are being developed for process monitoring. One of the most promising for liquid phase analysis is near-infrared spectroscopy (NIR) [11]. Use of fibre-optic probes and flow through cells makes in/on-line operation possible. Analysis is based on the overtones and combination bands from the –CH, –NH and –OH infrared vibrations for molecular groups present in

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[*] Corresponding author. Tel.: +46 132812586; fax: +46 13288969.
E-mail address: robbj@ifm.liu.se (R.B. Bjorklund).

[1] Present address: Scandinavian Biogas Fuels AB, Väderkvarnsgatan 14, SE-753 92 Uppsala, Sweden.

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the sample. Thus unlike most of the instrumentation used today in biogas processing plants, the NIR signal is related to the chemical and physical composition of the broth but is not specific for any individual components. A number of studies have shown the utility of the technique for monitoring different aspects of the biogas process [10,12–14]. Multivariate data analysis was used where data sets containing NIR (and sometimes other) variables were reduced by principal component analysis [15] into a few orthogonal components. These expressed most of the total variation as a way to simplify the interpretation of the large number of variables measured. The approach has proved successful for monitoring methanogen density [12], dry matter and total volatile fatty acids [13], acetate and microbial density [14] and early warning disturbances based on propionate [10].

Electrochemical measurements using electrode arrays is another non-specific analysis method which can generate information about the composition of liquids when data is treated with multivariate techniques. Such systems for non-selective sensing are suitable for in-line operation and capable of performing both classification of complex bioprocessing liquids and quantitative prediction of individual components [16,17]. Voltammetry using noble metals is a particularly robust analysis system where application of potential excursions generates clean and reproducible electrode surfaces [18]. The technique can be applied in several modes. Pulse voltammetry based on the rate of decay of charging and Faradaic currents following a potential step offers a non-selective method for monitoring changes in electrolyte composition with respect to ionic and redox active species. The goal of the study reported here was to evaluate the stability of noble metal electrodes during pulse voltammetry in a biogas broth and to determine if qualitative trends in concentrations of ionic and redox active compounds could be followed over time. The sensor can generate a large amount of data with respect to current responses as a function of potential, pulse time and electrode type. The electrode sensor array has been previously shown, after calibration with reference analyses, to be capable of delivering quantitative predictions of pH, COD and bacteria colonies [19–21]. There is thus potential for the system to offer a low price alternative for several of the instruments presently used for process monitoring.

2. Experimental

The sensor probe consisted of four 1 mm diameter metal wires (Au, Pt, Rh, stainless steel (GoodFellow, UK)) embedded in dental material Filtek^{TM} (3M, USA) and housed in a stainless steel cylinder having outer diameter 15 mm. Copper leads were soldered to each electrode wire and they were positioned in a plastic disc which was inserted into one end of the cylinder with about 3 mm of each electrode exposed. The space between the disc and the end of the cylinder was filled with Filtek^{TM} and hardened by exposure to UV light. Electrodes were wet polished with SiC grinding paper (P4000, Wirtz Buehler, Germany) resulting in the probe surface shown in Fig. 1.

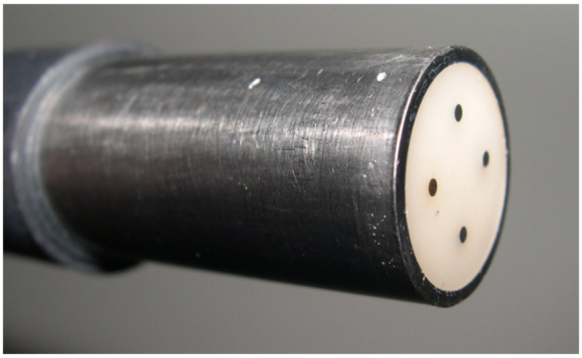

Fig. 1. Sensor probe housing and electrodes.

Sensor data was generated by pulse voltammetry using an in-house potentiostat controlled by DXE software from Proxedra (Linköping). The auxiliary electrode for each sensor (also called the reference electrode in a two-electrode cell configuration [22]) was the stainless steel probe housing having an area of about 3 cm^2 when immersed in the broth. The normal pulse sequence employed started at −1.2 V and increased at 0.4 intervals to +1.2 V with 0.0 V pulses between each interval. Pulse time was 250 ms. A cleaning step was performed before each pulse sequence consisting of 1 s at +0.5 V, 1 s at −1 V and 3 s at 0 V. Measurements were made continuously but only stored at 20-min intervals. The voltage pulse sequence employed was designed to cover a wide range of potentials for generation of charging/discharging currents from ions and Faradaic currents from redox active compounds in the reactor liquid. Since no standard glass reference electrode was employed, the exact potentials of the working electrodes were not known. This was not a significant problem with respect to generating current response patterns since the purpose of the study was to follow relative changes in the broth. The area of the auxiliary electrode was large and thus did not limit the currents flowing at any of the potentials.

The bioreactor was constructed from a 4-l glass vessel (Luminarc, France) that was equipped with a propeller for mixing. The inoculum was a manure culture. After inoculation, the vessel was placed in a water bath at a temperature of 37 °C. Substrate was introduced once daily in slurry form and was on the order of 2 kg VS/m^3, where VS is volatile solids, organic matter which can be converted to gas. The output gas volume from the reactor was measured with gas meters (Technical University of Hamburg, Germany) based on the principle of water displacement. The sensor probe was positioned in a tube extending into the reactor with the electrodes about 1 cm below the liquid level. Measurements for both the sensor and gas production were started on the fourth day after inoculation.

Individual current responses were followed over the course of the 32-day production in order to indicate specific trends in the collective electrochemical properties of the broth. Multivariate data evaluation was also performed using the DXE software from Proxedra. Principal component analysis based on all the current responses was used to follow the daily sensor description of changes in the reactor content. The X-matrix for the daily analysis was filled with about 70 rows from the sensor measurements and 3 × 120 columns of sensor current responses (responses from Au electrode not used because of sulfide fouling as described in Section 3). Score plots of principal component (PC) 2 vs. PC 1, the two components which described the largest structural variation in the measurement set, were a convenient way to visualize the daily variations in the broth.

3. Results and discussion

Applying voltages to the electrodes resulted in current responses corresponding to charging and Faradaic currents related to the compounds present in the reactor. Fig. 2 shows responses for the two largest voltages. The negative potential produced a current response which leveled off with time and did not return to zero for the Pt and Rh electrodes, indicating that both positively charged ions and reducible redox active compounds were present in the reactor liquid. For the noble metals the current response from the +1.2 V pulse quickly returned to zero for the Pt electrode but exhibited a small current after 250 ms for Rh. This indicated that

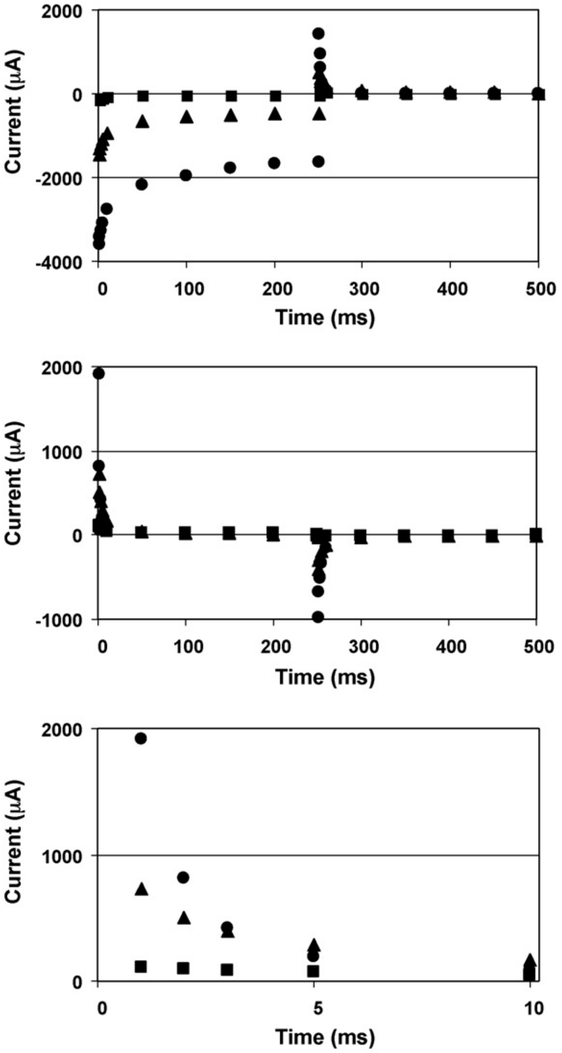

Fig. 2. Current responses during application of −1.2 V (1–250 ms) and 0.0 V (251–500 ms), upper; +1.2 V (1–250 ms) and 0.0 V (251–500 ms), middle; and +1.2 V during first 10 ms, lower, for platinum (circles), rhodium (triangles) and stainless steel (squares) electrodes.

redox compounds were oxidised on the Rh electrode but not the Pt. Discharging currents at 0 V for both potentials quickly returned to zero.

The basis for the pulse voltammetry technique is the difference in the rate of the decay of the charging and the Faradaic currents following each potential step. Since the charging current decays exponentially, its rate of decay is much faster than the Faradaic current which decays as a function of $1/(\text{time})^{1/2}$. Thus in an electrolyte containing only ionic species current responses upon applying potential steps to an electrode will quickly decay to zero after a short time (defined as 5 × time constant for the electrochemical cell). In the event compounds which can be oxidised or reduced at the applied potentials are present the measured currents at longer times will be solely the Faradaic current related to those redox species. These features are illustrated in Fig. 2 where the current responses for +1.2 V applied to the electrodes decayed rapidly whereas the responses for the −1.2 V potential exhibited Faradaic currents at longer times. The decay in discharging currents which started at 250 ms when 0 V was applied was rapid for both. Differences in current response decay for the different electrodes were observed at shorter times during the +1.2 V pulse as shown at the bottom of Fig. 2. This indicated that rhodium registered a slightly higher Faradaic current than the others but the conclusion from the figure is that only low concentrations of compounds which could be electrochemically oxidised at +1.2 V were present in the broth.

The Faradaic currents at longer times during the −1.2 V pulse indicated that compounds which could be electrochemically reduced by the electrodes at that potential were available in the broth. At atmospheric conditions the dominant electron acceptor in electrolytes is oxygen. In the closed reactor any oxygen introduced with substrate would have been quickly consumed and the biogas process was maintained at anaerobic conditions. Methanogenesic respiration uses alternative electron acceptors such as dimethylsulfide, nitrates, ferric ion and carbon dioxide. The latter is the dominate terminal electron acceptor in the process. Pyrosequencing of a bioreactor DNA sample has indicated that archea related to *Methanoculleus* use carbon dioxide as electron acceptor and hydrogen as electron donor to produce methane [23]. Carbon dioxide has also been shown to be an electron acceptor electrochemically both with respect to electrosorption [24] and electroreduction [25,26]. This property has been used to produce methane by electromethanogenesis [27] and thus, in the absence of dissolved oxygen, the currents shown in Fig. 2 for the −1.2 V pulse may have a contribution from reduction of the carbon dioxide in the broth.

The complexity of the biogas slurry results in the current responses describing the collective electrochemical properties of the broth and not specific compounds. The variations in the current responses shown in Fig. 2 are the result of the differing electrode properties of the metals in the sensor. For noble metal electrodes the surface is covered by hydride or oxide films at different potential ranges [28]. The active surface of an electrocatalyst interacting with adsorbed species is thus dependent on the applied potential. The electro-oxidation and -reduction of organic compounds, an important component of our sensor system, has been shown to be dependent on oxide coverage, for example occurring at potentials where no oxide is formed on gold for methanol but only with oxide coverage for malic acid [29]. In addition, anions in the reactor liquid such as chloride and sulfate can modify electrode activity and by-products of electrode reactions can influence reaction rates as is the case for strong carbon monoxide adsorption on platinum during methanol oxidation [28].

Reactor operation during the test period is shown in Fig. 3. Loading was maintained at about 2 kg VS/m^3/day. Gas production leveled off above 4 l/day 5 days after the measurements started. No substrate was introduced on day 25. This disturbance resulted in a temporary decrease in gas production followed by an increase to higher levels.

Plotting individual current responses (for example, the response at 2 ms during the +1.2 V pulse) over time gave electrode specific information about the electrochemical properties of the broth during production, Fig. 4. The response for the Au electrode (not shown in Fig. 4) increased for 3 days reaching a value of about 700 μA at measurement 200. It then decreased rapidly leveling off at about 90 μA where it remained for the rest of the test period. Some daily oscillations corresponding to feeding cycles were observed. The electrode was coated with a black film when the sensor was removed from the reactor indicating fouling by sulfur compounds. Modification of metal electrodes by adsorption and reaction with sulfur compounds has been known for some time and Au surfaces form strong bonds with S [30]. Both spontaneous deposition and potential related deposition/dissolution processes have been observed by electrochemical quartz microbalance experiments in the Au–S system [31]. Thus it is not surprising that the current responses from the Au electrode exhibited a significant decrease after 3 days in the biogas broth and only intermittent oscillations during feeding cycles thereafter. Although the current responses from the fouled electrode may have contained some information

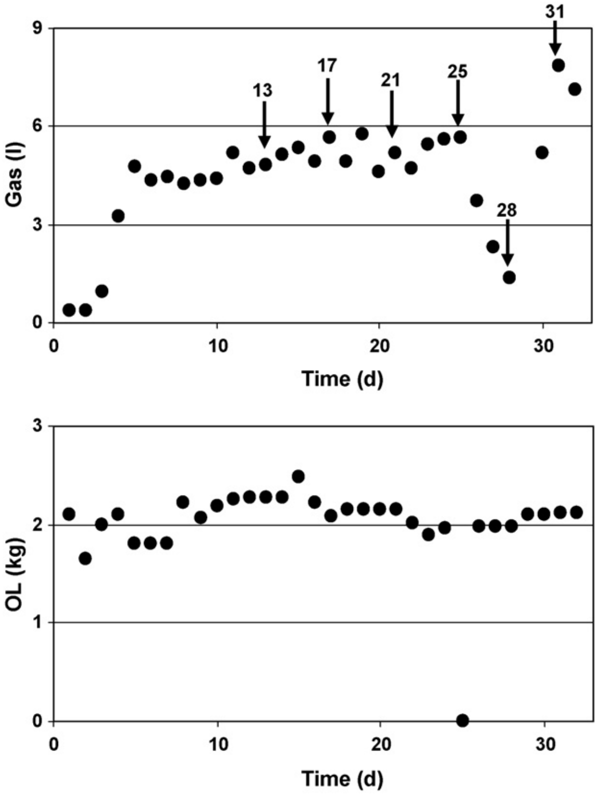

Fig. 3. Daily gas production (upper) and organic loading (OL, lower). The sensor measurements were concluded during day 32. Days highlighted along the gas production curve are discussed later in the text.

about the biogas process, it was decided to exclude them from the multivariate analysis.

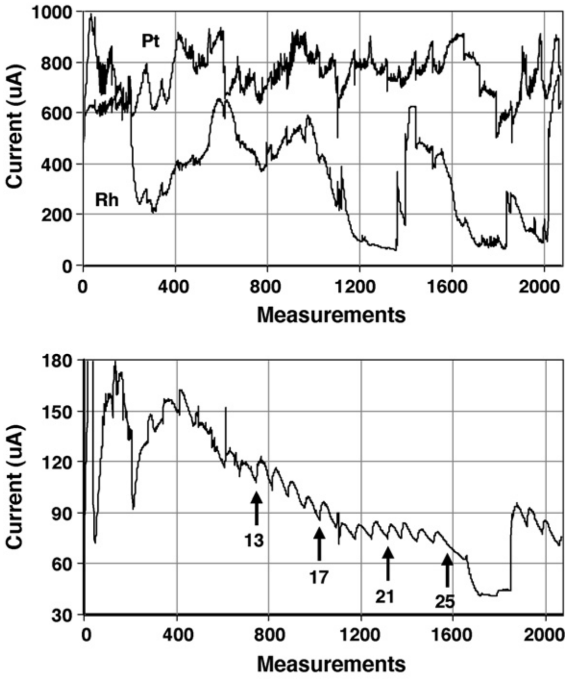

Fig. 4. Current responses for the +1.2 V pulse at 2 ms during 32 days of biogas production. Nineteen hours of measurements were not recorded at measurement 1103. Days described in Fig. 6 are indicated along the stainless steel response curve.

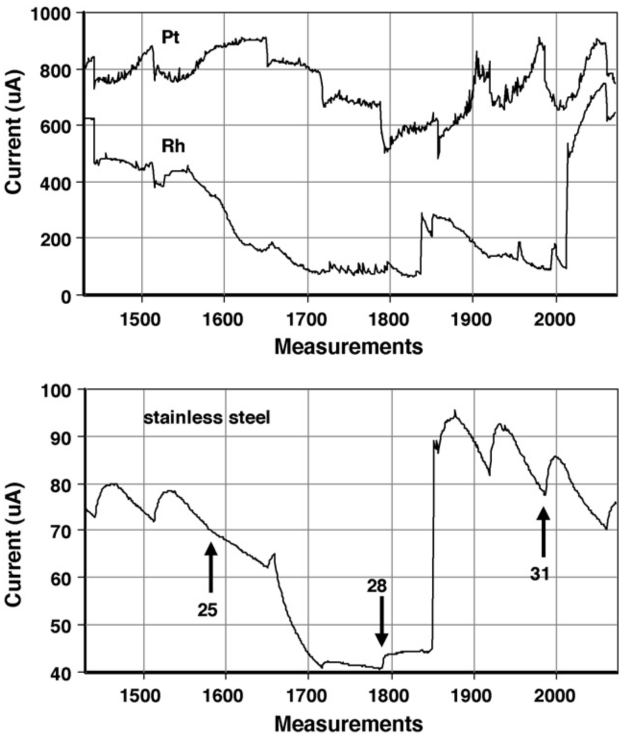

Fig. 5. Current responses for the +1.2 V pulse at 2 ms during the final 9 days of measurements. No substrate was added during day 25, measurements 1580–1651. Days discussed in the text are indicated along the stainless steel response curve.

The current response for stainless steel at 2 ms for +1.2 V shown in Fig. 4 was also lower than for Pt and Rh but it was consistently low from the beginning and exhibited a distinct oscillation related to the feeding cycles during the test period. Since the chromium component in 300 series stainless steel (AISI 302 (Fe/Cr18/Ni8)) forms a protective oxide layer it is not surprising that current responses for the stainless steel electrode were lower than for Pt and Rh. The protective oxide layer is also less reactive toward sulfur than Au. Stability in biogas broth has been reported for coupons with only some localized corrosion being observed after 20 days in a biodigester having sulfide concentration of 17 μM [32]. Mild steel samples in the same test solution were observed to be covered by a black film where one of the components was believed to be FeS.

The response for the Pt electrode was in a narrow current range, in contrast to that of Rh which exhibited three current decreases to about 100 μA (at measurements 1300, 1700 and 2000). These may have been caused by temporary electrode fouling since recovery was quite rapid in each case. However, similar behavior has been observed for Rh during monitoring of yoghurt fermentation with no indication of fouling [33].

Substrate was omitted on day 25 and current responses before and after the omission are shown in Fig. 5. Substrate would have been added at about measurement 1580 which is defined as the start of day 25. The curves shown in the figure start 2 days before with the diurnal oscillations clearly shown for the stainless steel responses. Oscillations are also seen in the Pt and (to a lesser extent) Rh responses during this period. The introduction of substrate resulted in sharp decreases in current for the Pt electrode. The oscillation related to substrate introduction was not seen on day 25 and resumed again the following day at measurement 1651, most clearly seen for the Pt responses. The substrate omission resulted in a decrease and then increase in gas production, as shown in Fig. 3, and this recovery period was described differently by each electrode. The current generated by the Pt electrode decreased until the third day after the substrate omission (day 28 in Fig. 5) and then increased gradually. The Rh current initially decreased, exhibited a maximum on day 28, and increased sharply on day 31. Current

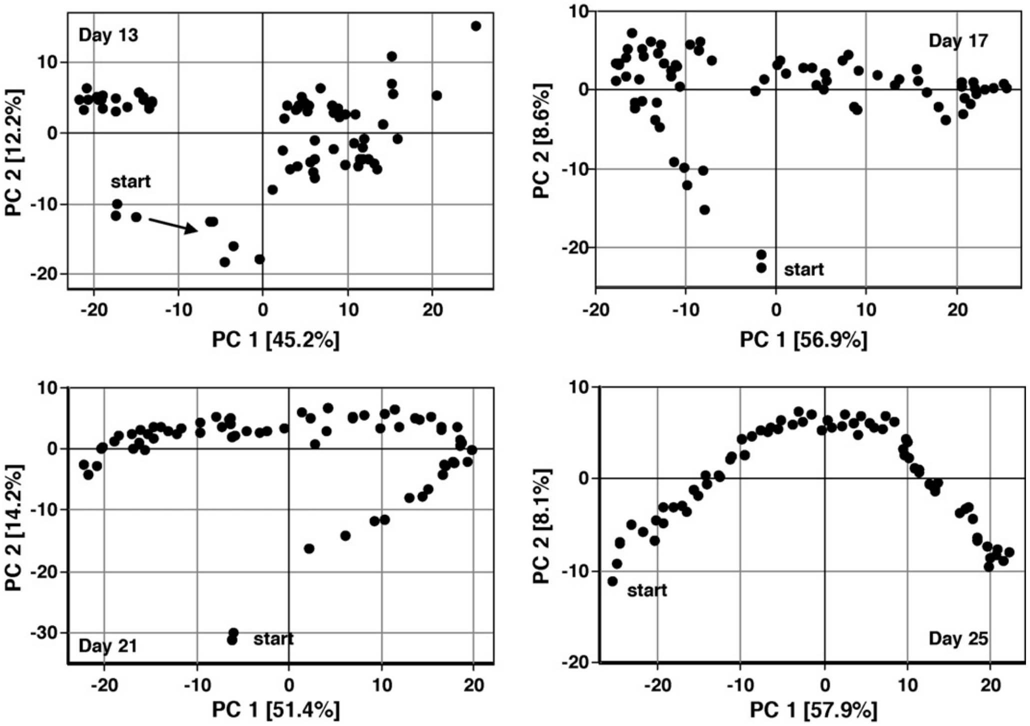

Fig. 6. Score plots describing the variability in the current responses during days 13, 17, 21 and 25 (as indicated in Fig. 4). Start is at introduction of substrate and points are at 20 min intervals, each plot corresponding to about 24 h. Variance scaling was used.

response for the stainless steel electrode recovered sharply towards the end of day 28 to levels higher than before the substrate omission. The feeding cycle oscillations during the final 3 days became well pronounced for the stainless steel electrode. These results are difficult to explain without further information about the status of the reactor after the substrate omission. However, they may indicate that the electrodes were sensitive to different aspects of the biogas process and how a period of low substrate availability affected concentrations of the metabolic products generated by the microbial groups present.

Figs. 4 and 5 show the description of events in the broth obtained by following 1 of the 360 current responses generated by each measurement. A more complete characterisation of the broth electrolyte is contained in the total responses. Multivariate data evaluation is necessary to extract relevant information from such a complex data set. Principal component analysis is a convenient way to visualize how all the responses described the liquid phase during substrate consumption. Fig. 6 shows score plots corresponding to diurnal substrate consumption. The principal components described the variance in the responses, accounting together for 57–66% of the total variance for the different days.

The principal components shown in Fig. 6 are not related to specific compounds but rather describe collective electrochemical properties of the broth [15]. Since the charging currents dominated responses, as shown in Fig. 2, it is reasonable to relate PC1 to the conductivity of the liquid. PC2 can then be assigned to redox active compounds with carbon dioxide being a dominant electron accepting species at negative potentials. Carbon dioxide concentrations in reactor headspace increase upon substrate addition [14,34] and have been reported to reach a maximum after about 5 h in a reactor operated with daily substrate introduction [34]. Upon introduction of substrate, movement along both principal components was observed for all the days. During days 13, 17 and 21 the movement along PC2 could be related to an increase in dissolved carbon dioxide. Since introduction of substrate also resulted in increases in organic acid concentrations [9], the movement along PC1 could have been the result of increased concentrations of these ionic compounds. After about 5 h, movement along PC1 reversed indicating a decrease in organic acid concentration as they were consumed by the process [9]. Little movement was observed in the PC2 direction as dissolved carbon dioxide levels stabilized. Day 25 exhibited a different behavior. With no introduction of substrate to drive the process, movement along PC1 was possibly related to continued consumption of organic acids while PC2 movement was related to a concentration oscillation of redox active species during the period.

Electrode specific score plots were also generated from the current responses. The plots retained the forms shown in Fig. 6 with the current responses for Pt showing a decrease in variability accounted for by PC1. Plots generated from the responses for Rh and stainless steel exhibited increases in variability accounted for by PC1, relative to the plots in Fig. 6.

The information available in Fig. 6 describes the variability in the current responses. Relating these to the collective concentrations of ionic compounds and redox active species in the broth provides a framework for describing the qualitative changes that occurred when substrate was introduced and consumed. As qualitative pathways describing individual feed cycles they may have application in process fault detection. This has been demonstrated for microbiological processes such as monitoring of wastewater treatment in both continuous [35] and batch modes [36]. The next step to quantitative monitoring would require extensive analysis for specific compounds to use as reference data in linear regression models for predicting concentrations of intermediate metabolic products [16]. These could be species in the liquid phase such as acetate and propionate and even correlation between the sensor's current responses and concentrations of volatile fatty acids in the gas phase could be tested. Carboxylate anions adsorbed on electrodes participate in the Kolbe electrosynthesis reaction at high anodic potentials, competing with oxidation of the solvent in a decarboxylative dimerisation with carbon dioxide as by-product [37,38]. Since little Faradaic current was observed at the relatively low anodic potentials used in this study there is the possibility that higher potentials would generate information specific to the acids present in the broth electrolyte. Such high potentials could detrimentally affect electrodes and may necessitate the use of materials with enhanced stability such as conductive-diamond [39] or bimetallics to increase electrocatalytic activity [40].

At the current stage of development it is premature to compare the electrode array sensor with more established techniques but it has a number of features in common with NIR. NIR has found applications in a number of diverse fields [41]. It is a rapid technique with multiple scans and data processing being performed in less than a minute. Molar absorptivity in the near-infrared region is low. While this limits the sensitivity of the technique to about 1000 ppm concentrations, it allows penetration further into a sample than can be attained with mid infrared radiation. The penetration property combined with good transmission of fiber optics in the near-infrared has enabled in-line process monitoring of liquids by fiber optic probes. Use of multiplexers makes possible measurements at several process points by one spectrometer. Since the technique is non-specific, quantitative information can only be obtained after calibration based on known concentrations of compounds of interest using chemometric methods. As mentioned in the introduction NIR has been applied to monitoring different properties of the biogas process [10–14].

The voltammetric sensor probe compares favorably with several of the NIR features. The method utilizes voltage amplitudes and current response times instead of selected wavelengths to obtain comprehensive information about a liquid sample. It monitors the electrochemical properties of the broth electrolyte in contrast to NIR which measures the chemical signatures of the species present. Voltammetry measurements and data treatment can be performed on the order of a minute. The low cost of the probes makes possible multiplexing with several probes in the reactor controlled by a single PC. Since electrochemical reactions occur on electrode surfaces the effective sampling volume of the probe is more limited than for the NIR technique. Fouling of fiber optic probes may necessitate removal and cleaning but the electrode array can be cleaned by self-polishing while in contact with the electrolyte [42]. Both methods require labor-intensive calibration and validation prior to being used for quantitative analysis. Since no such calibration was done in this study there is only a potential for quantitative analysis by the probe based on examples from other applications where relevant biogas parameters have been quantitatively predicted using linear regression models. These include cationic demand and turbidity in the wet-end of a paper machine [19], microbial growth in pulp [20] and COD, conductivity and pH in paper mill effluent [21].

4. Conclusions

The results from the study demonstrated that voltammetric measurements can monitor the liquid phase of a biogas reactor for an extended time. Visible surface fouling was only observed for the Au electrode which was not included in the analysis. Following individual current responses over time gave an overview of the biogas broth with each electrode metal providing a different perspective of the biogas production. Stainless steel was most sensitive to the daily fluctuations associated with the introduction and consumption of substrate. Platinum indicated stability in the process whereas rhodium followed changes in the broth at repeated intervals. Current responses from all three metals described the omission of substrate as a disturbance in the process followed by a recovery. Multivariate treatment of the data by principal component analysis using all current responses described the daily feed cycles as initial increases in redox active species and ionic compounds for about 5 h followed by constant redox specie concentrations and decreasing ionic compound quantities. The results could be related to qualitative monitoring of initial production of carbon dioxide and organic acids upon substrate introduction followed by later consumption of the acids and stabilisation of dissolved carbon dioxide concentrations in the broth.

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