Evaluating the use of Inverse Gas Chromatography to Characterize the Surface Properties of Petroleum Coke and Recycled Anode Butts in Pre-Baked Carbon Anodes

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Abstract

Carbon anodes are used in the production of Aluminum, which is used in our everyday lives. These carbon anodes are composed of three materials: the solids, which are petroleum coke and recycled anode (butts); and the liquid, or binder, which is pitch. When bound together, it has been found that the pitch adheres more so to the recycled anode material than the petroleum coke. The research project focused on trying to determine why this is so with the use of inverse gas chromatography to evaluate the surface properties of the two solids. Inverse gas chromatography allows various gases to react with each raw material surface, thus allowing the surface properties, such as surface tension and acid-based properties, of the material to be determined. The main part of this project entailed proving that the inverse gas chromatography is useful in determining the surface properties of these raw materials. Since inverse gas chromatography was a feasible method, the raw materials were tested. The petroleum coke material was fully characterized, but the recycled anode material was not due to uncontrollable circumstances.

Introduction

Aluminum is a universally utilized material. Aluminum also has a variety of well-known uses, such as the manufacturing of soda cans, jewelry, pots, pans, and aluminum foil. It has even been applied in the construction of jets and airplanes. Aluminum has also been used in a variety of technical settings such as electrical wiring, the manufacturing of microchips, in door and window frames, as well as in the construction of bridges and building foundations. Aluminum can be molded in numerous ways, such as rolling, which is squeezing the aluminum between two rollers to form a flat plate sheet or foil product at very fine gauges; casting, which is pouring molten metal into molds; and pressing, which is forcing a flat metal blank into a die under a press from a metal ram, mainly used to manufacture 'holloware' [1]. Before any of these things can be done with the aluminum, it has to be processed into a usable form.

The production of commercial aluminum involves the Hall-Heroult smelting process. This smelting process is an electrochemical process where calcined aluminum oxide (Al₂O₃) is dissolved in a bath of molten cryolite (Na₃AlF₆). Aluminum is formed by cathodic reduction and the carbon is oxidized at the anode to form carbon dioxide (CO₂) [2].

Approximately 470 kg of carbon are used to manufacture about 1000 kg of metal. Carbon, which is in the form of anodes, makes up about 25% of the production cost of
aluminum. The cost contribution in the production of aluminum is primarily that of the raw materials. The anodes are consumed during the electrolysis process and must be replaced every 14 to 28 days depending upon the size and density of the anodes, and the opening parameters of the cell. Carbon anodes also present a source of electrical resistance in the cell, thus they contribute to the cost of electricity [2].

The production of carbon electrodes has been discussed in detail elsewhere [2]. A summary is provided below.

A carbon anode is composed of three parts: two solid fillers and a liquid, or binder. The filler material used in the manufacturing of carbon anodes is called coke and is a product of the delayed coking process. Coke is a hard, gray, massive fuel prepared by the destructive distillation of coal [3]. Carbon anodes are also composed of recycled anode material called butts. Butts are the remains of a carbon anode after it has been in a cell for three weeks. Recycled anode material must be reused in the anode production process due to economic purposes. The binding material used in the production of carbon anodes is a by-product of the destructive distillation of coal, or the coke-making process. Coal tar is converted into pitch by a refining process that includes distilling the tar until its residue has the desired softening point. The function of pitch in the manufacturing of anodes is to provide a bond between the pieces of filler material to hold the structure together and to provide electrical contact. The pitch must be able to wet the aggregate particles, fill the pores of the anode to some extent, and yield a strong dense coke bond between the particles.

There is circumstantial evidence that there is a difference in the wetting and penetration behavior of the pitch between the petroleum coke and recycled anode particles. One suggestion is the difference in pitch demand accounted for separately by Belitskus [4] and Proulx [5]. Both observed that the absence of recycled butt particles in an collective formulation increases the optimal pitch level by about 1% comparative to the level required with the butt particle contents normally used in factories, which ranges from 18% to 20%. Another suggestion is the difference in the thickness of the pitch film coating particles found by Adams [2]. The characterization of the surface properties of the filler materials could help explain this behavior.

One technique that has been used to characterize carbon materials is inverse gas chromatography. Chromatography was first introduced by Russian botanist Mikhail Tsvett in his process of separating highly colored compounds, thus the name meaning ‘color recording’ [6]. Gas chromatography (GC) is a version of this. GC is a system that consists of liquid with a high boiling point infused on an inert solid support as the stationary phase and helium gas as the mobile phase.

The stationary phase of the process is a thin metal column packed with a solid in which the helium gas is allowed to flow through. The column is attached to an injection port and the entire system is heated in an oven. The liquid is injected into the column through the injection port by a syringe and is immediately volatilized. The helium gas then carries the liquid out of the column and past a detector.

Characteristics, such as polarity and volatility, of the liquid determine how long it is retained by the column. When each liquid passes the detector, a peak is registered on a recorder, which is usually a computer monitor. The comparative quantities of the components can be established by the areas underneath the peaks. Other conclusions can be determined by varying the polarity and temperature of the system. In this process, the
properties of the solid compacted in the column are already known. The properties of the mixture of the substance injected are what are going to be determined and are based upon the height of the peaks recorded and the retention time. The retention time is the time the injected solute spends inside of the GC column. These components are dependent upon the properties of the liquid and how it reacts with the solid.

Inverse gas chromatography (IGC) utilizes the same processes as gas chromatography. The differences are in what is known and what is not, and what is injected. The properties of the solid phase that is packed inside of the column are unknown, but the properties of the gas or liquid that is injected are known. In IGC, one component at a time is injected into the injection port and a peak is recorded when the component reaches the detector. Injecting various molecular probes into the column and recording their retention times allows the properties of the solid in the column to be characterized. Gas chromatography aids in characterizing the molecular probes injected into the chromatograph, while inverse gas chromatography aids in the characterization of the solid compacted into the column.

**Purpose**

The aim of this research is to characterize the chemical surface properties of the two solid raw materials using inverse gas chromatography. The objectives in carrying out this research are four-fold:

1) To asses the feasibility of obtaining reproducible results using inverse gas chromatography using a syringe.
2) To establish a methodology for evaluating carbon anode raw materials.
3) To characterize the dispersive surface properties of the raw materials.
4) To compare and contrast results from the two different raw materials, petroleum coke and recycled butts.

**Methodology**

Approximately five grams of filler material, sized to –60+100 mesh were custom packed into a 1.5m x 2 mm stainless steel GC column by Restek Corporation. Each column was put into a Hewlett Packard 5890 series II gas chromatograph with a flame ionization detector. Helium was used as the carrier gas at a flow rate of approximately 20 ml/ min. The column was conditioned to 150°C for 48 hours prior to the initial analysis. The column was then heated for at least 12 hours at the desired analysis temperature under a continuous flow of helium at approximately 20 ml/min before each run. Three-tenths of a microliter to 0.5 microliters (µl) of each sample were injected into the column and the retention time was calculated based on the peak of the symmetrical elution curve.
Results and Discussion

Objective 1: To assess the feasibility of obtaining reproducible results using a gas chromatograph.

The first objective of this project was to determine whether or not inverse gas chromatography with syringe injection is a feasible procedure in the characterization of the chemical surface properties of the raw materials, i.e. petroleum coke and recycled anode butts. Previous experiments using inverse gas chromatography had not been successful. Other researchers have reported that injecting various volumes of a 0.1 ml solution, using coal surfaces, resulted in retention times that varied with the injected volume. In one occurrence, the use of a sophisticated vacuum loop was required to obtain infinitely diluted solutions [7].

Two factors, one practical and one theoretical, limited the determination of a suitable injection volume. The practical limitation was that the injection volume had to end with a retention time that is within the measurable limits of the chromatograph. The theoretical limitation was that the injection volume had to be in the Henry’s Law region, which would make any interactions other than gas-solid insignificant. These limitations are surpassed when the recorded peaks are symmetrical and the retention times are independent of the volume that was injected.

Three variables were adjusted to deal with these limits: volume of the sample in the vial, which is the initial concentration of the gas; volume of the sample injected from the vial, which is the injected volume, and the detector signal attenuation. The injection volume was determined systematically by adjusting these three parameters until the detection requirements were met. The samples were injected at volumes of 0.2 to 0.5 µl, to ensure that the retention time did not vary with the injected volumes.

Using two molecular probes, chloroform (CHCl₃) and hexane (C₆), the reproducibility and symmetry of the peaks were tested. The gas chromatograph was heated to 150°C. Each probe was preheated to 125°C and 0.3 µl were injected. The recorded peaks all fell within a voltage range of 10 mV of each other, on a graph of time versus voltage. Also, the retention times all fell within a 0.5 second range from the longest to the shortest times recorded. Then, 0.5 µl of each probe were injected into the gas chromatograph to determine if the retention times varied with the injected volumes. The retention times from this volume deviated no more than 4% from the retention times from the 0.3 µl injection. All of these values landed within the 95% confidence interval of each probe.

Objective 2: To establish a methodology for evaluating carbon anode raw materials.

The second objective of this experiment was to establish a method to evaluate the surface properties of the filler materials. Originally, for the petroleum coke experiment, the temperatures in which the probes were to be tested were 150°C, 200°C, 250°C, and 300°C. This changed when it was found that the max temperature of the gas chromatograph is 265°C. The final temperatures of the gas chromatograph (GC) were 150°C, 200°C, 250°C, and 265°C. At 150°C, it can take a probe up to 10 minutes to reach the detector in the GC and the recorded peaks were broad. Any temperature lower than
150°C would cause slower results. Thus, only temperatures 150°C and above were used for testing. The recycled anode material was originally supposed to be tested at the same temperatures as the petroleum coke material. Those temperatures were changed to 150°C, 175°C, and 200°C. This was because the recycled anode material had gone through electrolysis and its surface began to burn off along with the injected probes when the temperature was set above 200°C. For each set of probes, the GC was set at each temperature and allowed to condition overnight.

Eleven molecular probes were used to test the surface properties of the raw materials. A series of \( n \)-Alkanes was used to test the dispersive properties and the polar probes were used to test the acid-base properties. These probes are listed in the following table:

<table>
<thead>
<tr>
<th>( n )- Alkanes</th>
<th>Polar Probes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>Chloroform</td>
</tr>
<tr>
<td>Pentane</td>
<td>Dichloromethane</td>
</tr>
<tr>
<td>Hexane</td>
<td>Toluene</td>
</tr>
<tr>
<td>Heptane</td>
<td>Diethyl Ether</td>
</tr>
<tr>
<td>Octane</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td></td>
<td>Carbon Tetrachloride</td>
</tr>
</tbody>
</table>

Each probe was placed into a 10 ml GC auto sampler headspace vial with a pressure release silver seal and PTFE/Silicone septum. The samples were heated to 125°C, with the exception of n-octane at 135°C, for 30 minutes. The volume of gas injected was 0.3 µl with the use of a 0.5 µl SGE gas-tight syringe.

Objective 3: To characterize the dispersive and acid-base surface properties of the raw materials.

Two thermodynamic factors were calculated using the data collected from the IGC: the heat of adsorption of each sample \( \Delta H_a \); the dispersive component of the surface tension, \( \gamma_s^d \). Each of these was based on the retention volume, \( V_g \), and properties of each sample.

\[ V_g = \frac{V_o(t_r - t_m)j}{W} \]

Where:
- \( V_g \), corrected retention volume (ml/g)
- \( V_o \), flow rate of the carrier gas (ml/min)
- \( t_r \), retention time of the molecular probe (min)
- \( t_m \), retention time of the non-absorbing marker, which is methane (min)
W, weight of the stationary phase, the raw material inside of the column (g)
j, the gas compressibility correction term

\[ j = \frac{3(P_i/P_o)^2 - 1}{2(P_i/P_o)^3 - 1} \]

Where:
P_i, inlet pressure (psi), or column pressure
P_o, outlet pressure (psi)

The heat of adsorption, \( \Delta H_a \), for each compound was calculated from the slope of the straight lines from the graph of \( R \ln(V_g) \), where \( R \) is universal gas constant (8.314 J/mol K) multiplied by the natural log of the corrected retention volume, versus the inverse of the temperature (1/T) on the Kelvin scale.

An example graph for chloroform and hexane is given below:

![Graph showing the relationship between \( R \ln(V_g) \) and 1/T for chloroform and hexane](image)

**Figure 1: Curve for calculating \( -\Delta H_a \)**

The calculations of \( -\Delta H_a \) for the remaining molecular probes are listed in the table below:
### Table 2: $\Delta H$ and $r^2$ of probes for petroleum coke.

<table>
<thead>
<tr>
<th>Molecular Probes</th>
<th>$-\Delta H$ (kJ)</th>
<th>$r^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>14.79</td>
<td>0.99</td>
</tr>
<tr>
<td>Pentane</td>
<td>23.09</td>
<td>0.96</td>
</tr>
<tr>
<td>Hexane</td>
<td>39.50</td>
<td>0.92</td>
</tr>
<tr>
<td>Heptane</td>
<td>33.95</td>
<td>0.99</td>
</tr>
<tr>
<td>Octane</td>
<td>30.83</td>
<td>0.80</td>
</tr>
<tr>
<td>Chloroform</td>
<td>24.81</td>
<td>0.99</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>67.03</td>
<td>0.95</td>
</tr>
<tr>
<td>Toluene</td>
<td>46.63</td>
<td>0.99</td>
</tr>
<tr>
<td>Diethyl Ether</td>
<td>42.29</td>
<td>0.99</td>
</tr>
<tr>
<td>Tetrahydrafuran</td>
<td>46.18</td>
<td>0.98</td>
</tr>
<tr>
<td>Carbon Tetrachloride</td>
<td>13.38</td>
<td>0.96</td>
</tr>
</tbody>
</table>

The dispersive surface tension, $\gamma_s^d$, expresses the potential of a solid to undergo dispersive types of interactions. Dispersive interactions occur when two non-polar molecules interact. One molecule goes into a dipole moment, meaning its electrons are rearranged to give it a charge. This molecule polarizes the other and thus, they are attracted [9]. $\gamma_s^d$ is estimated using the retention volume of a series of n-alkanes injected into the column [10]. It is calculated by the following relation by Doris and Gray [10]:

$$\gamma_s^d = \frac{(\Delta G_{CH_2})^2}{4\gamma_{CH_2}(Na)^2}$$

Where:

- $\gamma_{CH_2}$, surface free energy of a compound consisting of entirely $-CH_2$ groups
- $\gamma_{CH_2}$ is calculated using the following linear equation:

\[
\gamma_{CH_2} = -0.058 \text{ mN/m deg (T)} + B
\]

B is calculated first using $\gamma_{CH_2} = 35.6 \text{ mN/ m at 20^oC}$, which equates to a constant of 35.716. Then $\gamma_{CH_2}$ is calculated at each temperature in and Kelvin or Celsius [10].

The following is a chart of the dispersive surface tension of the coke material at 200°C, 250°C, and 265°C:

### Table 3: Dispersive surface property calculation for petroleum coke.

<table>
<thead>
<tr>
<th>Temperature ($^\circ$C)</th>
<th>$\gamma_s^d$ (N/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>0.1202066</td>
</tr>
<tr>
<td>250</td>
<td>0.1306864</td>
</tr>
<tr>
<td>265</td>
<td>0.1031233</td>
</tr>
</tbody>
</table>
area of a CH$_2$ group (0.06 nm$^2$) [10]

N, Avagadro’s number (6.022x10$^{-23}$)

$\Delta G_{aCH2}$, change in Gibbs free energy associated with a change in the number of CH$_2$ groups in a molecule

$\Delta G_{aCH2}$ is derived from the slope of the straight lines of the graph, where R is the ideal gas constant; T is the inverse temperature in Kelvin (1/T); and $V_g$ is the corrected retention volume. An example of this graph follows:

![Graph](image)

Figure 2: Curve for calculating $\Delta G_{aCH2}$

Objective 4: To compare and contrast results from the two different raw materials, petroleum coke and recycled butts.

The surface properties of the recycled anode material were not able to be characterized. The recycled anode butts material had gone through electrolysis prior to being packed into the column. When running the recycled anode butts portion of this experiment, much of the surface of the material was burned off. The samples were tested at 200°C and then the oven was set at 250°C overnight, approximately 16 hours. Within that 16 hour period, the signal was between 63 mV and 164 mV, when it is usually between 4 mV and 10 mV. The high signal meant that a substance in the machine was being read by the detector. Since no gas had been injected, the only thing left was the filler material in the column. Before the error had been detected, the samples were run at 150°C. When these values for the coke and the butts were graphed, the numbers were almost identical, thus proving that the recycled anode butts surface had been altered.
The following graph is a comparison of the corrected retention volume, \( V_g \), of the petroleum coke material to the recycled anode butts material at 200°C. There is a definite difference between the retention volumes of each surface. This comparison was not able to be made at the other temperatures due to the differences in the materials’ surface properties and error in the experiment.

![Retention Volume of Coke and Butts at 200°C](image)

Figure 3: Retention volume of coke and butts at 200°C.

**Conclusions**

Inverse gas chromatography was efficient in the testing and characterization of petroleum coke and recycled anode material. It is possible to obtain reproducible results with inverse gas chromatography using a syringe.

A methodology for using inverse gas chromatography was established and used to test the raw materials. This method was efficient and repeatable.

The dispersive surface properties of the petroleum coke were calculated and characterized. The same could not be done to the recycled anode material due to the error that occurred during experimentation. Due to this, a comparison or the surface properties between the two materials could not be completed.
Bibliography