Leaching kinetics of Oxides from Battery waste
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Introduction

Norway has the highest electrical vehicle (EV) fraction of new car sales in the world. Lithium-ion batteries (LIBs) have a long lifetime, in many cases above ten years, but eventually the batteries will reach end of life. Proper recycling then becomes an obvious requirement. The batteries used in EVs contain a number of valuable metals. For a sustainable environment, these metals need to be recovered and recycled. In this experiment, metals such as cobalt, nickel, manganese, iron and other valuable metals will be recovered employing leaching of crushed batteries from EVs. Crushed and powdered car batteries (mainly comprising cathode and anodes) are reacted with leachant, a mixture of sulphuric acid and hydrogen peroxide. The leaching kinetics of various metal oxides present in batteries are studied in this experiment.

The kinetics will be tracked by removing a small volume from the reaction mixture and analyzing it using UV-Vis spectrophotometer. Reactions parameters like temperature, concentration, solid/liquid ratio will be altered and the leaching will be studied as a function of these parameters and modelled adequately.

Theory

Leaching Experiment:

Leaching is a process where a soluble part of a solid dissolves into a liquid through a reaction at the interface between solid and the liquid. To understand the pathway through which these reactions proceed, a number of models have been developed. The models help in optimizing the process and help design equipment that can achieve efficient leaching at industrial scale.

One of the widely used models to study the leaching kinetics is called shrinking core model. Consider a solid A present in a liquid L and let us assume that the solid is spherical in shape. The reaction at the interface between the solid and liquid may proceed through one of the following ways,

a) The soluble part of the solid reacts and dissolves into the liquid. This leaves behind a shrinking core of the solid A that can eventually disappear.

b) The soluble part dissolves leaving behind an insoluble solid B which has the same size as A. The soluble part in A keeps on shrinking until the whole of A gets converted to B

c) The soluble part of A forms gelatinous layer around the shrinking core.
The kinetics of leaching can either be reaction-controlled (the surface reaction) or diffusion-controlled (diffusion of the solvable part). All leaching processes have both the processes but the overall kinetics will depend on one of these. The equations to calculate the rate constants of these two processes are given in the calculation section.

Figure 1: Shrinking core model [1]

**UV-Vis spectrophotometer:**

The instrument measures the absorbance of the material using the Beer-Lambert’s law which states that the quantity of the light absorbed by the substance in a solvent is directly proportional to the concentration of the substance and the path length of light travelling through the solution. The absorbance $A$ is given by,

$$A = \varepsilon lc$$

Where $\varepsilon$ is absorptivity of the species, $l$ is path length and $c$ is the concentration of the species.

**Experiment**

Each group will study the effect of one of the experimental conditions on the reaction kinetics. The different experimental conditions that will be studied are given in Table 1.
Table 1: Reaction parameters

When varying one reaction parameter, the other parameters used are highlighted. For instance, if a group works on understanding the effect of temperature, they should use S/L ratio 30, 3.75% $\text{H}_2\text{O}_2$ and 2M Sulphuric acid.

<table>
<thead>
<tr>
<th>Solid/Liquid Ratio (S/L) (g/L)</th>
<th>Vol % $\text{H}_2\text{O}_2$, y</th>
<th>Temperature, T (°C)</th>
<th>Concentration of Sulphuric Acid x, (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>3.75</td>
<td>40</td>
<td>1</td>
</tr>
<tr>
<td><strong>30</strong></td>
<td>5.60</td>
<td>60</td>
<td><strong>2</strong></td>
</tr>
<tr>
<td>50</td>
<td>7.50</td>
<td>80</td>
<td>4</td>
</tr>
</tbody>
</table>

Procedure

Prior to the experiment

- The parameter to be studied will be given by the supervisor.
- Learn about the chemicals used and the process, especially their hazards and safety.
- Prepare a work plan that should contain
  1. Theory about leaching and filtration, diffusion controlled and reaction controlled processes, shrinking core model.
  2. Experimental time plans showing calculations for solution preparation. Work distribution among group members.
  3. Understanding Leaching kinetic models and model graphs.
  4. A small section about the risks involved.
- The work plan should not be more than 2 pages.
- **The work plan should be submitted at least 3 days before the experiment day.**
• Read the risk assessment for the experiments.
• Maintaining a lab journal is good practice, a lab journal will be given to the group. Make sure to write down all the essential data and observation, including accidents and possible problems with the apparatus.

Experiments

Make sure all the glassware and the magnets used are clean. Prepare a sufficient amount of chemicals. Always use nitrile gloves while working with the chemicals. Inspect the setup for any damages or leaks and ensure all the connections are proper.

Startup

1. Materials
   a. Prepare 1 L of x (M) Sulphuric acid solution with y vol % of hydrogen peroxide.
   b. Weight out crushed battery waste in order to reach z S/L ratio for a total reactor volume of 250 mL.

2. Methods
   a. Setup the glass reactor on the stirring plate. Clamp it to ensure that the reactor is safely placed on the stirrer.
   b. Connect the water outlets to the reactor jacket and set the water bath temperature T (make sure that you have connected the correct outlets of water bath).
   c. Connect the condenser, clamp the condenser to ensure that it is safely placed in the reactor and turn on water flow for the condenser.
   d. As you wait for the temperature to stabilize, prepare your materials for the leaching experiments.
   e. Once the temperature has stabilized at the set value, put the magnetic stirrer in the reactor and add the crushed battery waste.
   f. Add 250 mL of x (M) Sulphuric acid with y vol% of hydrogen peroxide into the reactor and turn on the stirrer plate when you have added some acid and close the reactor.
   g. Start the stopwatch.
   h. Set the stirring speed at 500 rpm.
   i. Take samples of 2.5 mL after different time intervals i.e. 30 sec, 1 min, 1.5 min, 2.5 min, 5 min, 7.5 min, 10 min, 12.5 min, 15 min, 20 min, 25 min, 40 min, 50 min and 60 min respectively with pipette in small vials.
   j. Add the withdrawn sample into 2.5ml of DI water stored in a sample vial. This is done in order to quench, which will stop the reaction.
   k. Filter the 5ml sample using 0.45µm filter tips and store the sample for UV-vis measurement.
   l. While taking the samples, check and measure the temperature inside the reactor and note down the temperature of water in the reactor jacket as well.
   m. After 60 min, turn off the water bath, water flow in condenser and stirrer plate.
   n. Filter the remaining solution in the reactor by using a Buchner funnel setup using vacuum filtration.

3. Characterization of Samples
The samples are characterized using UV-Vis spectrophotometer.

For each sample, the absorbance will be measured for 3 wavelengths – 730nm, 515nm and 390nm.

The procedure to use the instrument will be shown at the lab.

The filter cake will be let kept for drying and the weight of the dried cake will be given the next day.

After the experiment:

1. Turn off the water bath and remove the magnetic stirrer and the temperature probe.
2. Carefully dispose of the waste and wash all the glassware properly.
3. DO NOT REMOVE THE WATER CIRCULATIONS – neither the reactor not the condenser.
4. Make sure the lab and the fume hood are clean for the next group.

Calculations

The equations \([2]\) for the shrinking core model when it is reaction-controlled reaction or diffusion-controlled reaction, are given as:

\[
1 - (1 - X)^{1/3} = k_c t \\
1 - 2/3X - (1 - X)^{2/3} = k_d t
\]

Where \(k_c\) is rate constant for reaction controlled and \(k_d\) is rate constant for diffusion controlled. \(X\) is the fraction of battery waste converted from metal oxide to metal sulphate. \(X\) is measured as a function of absorbance by using UV-Vis spectrophotometer at three different wavelengths i.e. 390nm, 515nm and 730nm.

Plot the absorbance as a function of time and use appropriate curve fit to the obtained data. Using equations above and fitting regression lines to data obtained from UV-Vis measurements, determine if the reaction follows a reaction or diffusion controlled pathway.

Report Guidelines

The report should address the following questions. The answers should be through understanding the process and explained using the data and results. The report should not directly answer the three questions, rather be evidence supported discussion.

1. Calculate and compare the leaching efficiency and leaching kinetics as a function of the parameter studied. Give reasons for the results obtained.
2. Find the rate constants \(k_c\) and \(k_d\). Find if the process is diffusion controlled or reaction controlled.
3. Discuss the reason for the observed temperatures (plot between temperature and time).
4. Reason for observed results between the experimental and modelling results.
Report:

The initial report should be submitted within a week after performing the experiments. The initial report should be complete with discussions, references, figures etc. After the feedback from the supervisor, the group will have one more week to address the feedback and submit the final version. The final report should also have a small abstract (less than 150 words). A section on other parameters that can be studied and why it should be studied and what can be expected from such studies can be included in the final report (for extra credits).

1. Title-page with small abstract, the title should indicate the experimental observation or results. (get creative)
2. Use Times New Roman 12pt with line spacing 2 for the initial draft.
3. Short introduction and theory followed by experimental work done.
4. Results with calculations and graphs.
5. Discussion about the results and relationships between the different experimental parameters.
6. Discussion about the experimental error (if any) and its effect on the final results.
7. Discussion about the different regression values obtained.
8. Literature references.
9. List of symbols and abbreviations.
10. An appendix with detailed calculations, Safety Datasheet, Risk assessment and copies from the lab journal.

Reference
