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Учебно-методическое пособие для студентов II курса специальности 1-48 01 04 «Технология электрохимических производств»

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Учебно-методическое пособие представляет собой комплекс текстов по химической тематике из оригинальных англоязычных источников и имеет своей целью развитие и совершенствование у студентов навыков различных видов чтения с выходом в устную речь в пределах предложенной тематики.

Предназначено для студентов II курса, а также магистрантов и аспирантов специальности «Технология электрохимических производств». Может использоваться и для обучения студентов III и IV курсов на факультете общественных профессий.

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предисловие

Пособие предназначено для студентов II курса, а также магистрантов и аспирантов специальности «Технология электрохимических производств». Оно может использоваться и для обучения студентов III и IV курсов на факультете общественных профессий по специальности референт-переводчик научно-технической литературы.

Учебно-методическое пособие составлено в соответствии с требованиями программы по иностранным языкам для неязыковых вузов. Его целью является совершенствование навыков чтения, понимания и перевода оригинальных текстов по специальности, а также развитие навыков устной речи в пределах предложенной тематики.

Пособие состоит из основных текстов, снабженных активным словарем и системой лексико-грамматических упражнений, и дополнительных текстов, содержащих новую информацию и связанных с тематикой основных текстов. Дополнительные тексты могут быть использованы при ведении бесед и для составления различных сообщений. При отборе текстов учитывались такие принципы, как информативность, предметная связность, доступность, соблюдение которых способствует расширению профессионального кругозора и усвоению определенного объема профессиональных терминов.

Материалом для данного издания послужили тексты, подобранные из американских и английских научных журналов, монографий и энциклопедий, содержащие профессионально значимую и познавательную информацию.

Использование пособия в учебном процессе позволит ускорить формирование у студентов навыков и умений, необходимых для чтения и реферирования научных текстов, а также будет способствовать повышению качества перевода литературы по специальности.

Данное издание может быть использовано как для аудиторных занятий под руководством преподавателя, так и для самостоятельной работы студентов.

PART I

ELECTROCHEMISTRY AS A SCIENCE

Electrochemistry is an important branch of science. It has contributed in many ways to our present understanding of the nature of matter. Electrochemistry is concerned with the interrelationship of electricity and chemistry, the close affinity of these subjects having first become clear from Faraday's studies of electrolysis published in 1833 and 1834. Electrochemistry deals, firstly, with the nature and properties of substances containing charged particles known as ions and, secondly, with the relationship between chemical reactions and electric currents.

Electrochemistry has provided valuable tools for scientific investigators and those working in the industrial and technological fields; it has given rise to developments on which much of our modern civilization depends. In the future electrochemistry can be expected to contribute even further to society's needs. The realization that the Earth's resources are finite must lead to an increased emphasis on the need to utilize these resources in such a way that wastage – and the associated pollution – are kept to a minimum. Electrochemical methods of producing industrial chemicals and energy have many advantages in this respect over more conventional methods even though much remains to be done before they can be fully exploited.

Active Vocabulary

affinity, electrochemistry, electrolysis, interrelationship, tools, matter, emphasis, advantage, to be concerned with, to contribute, to deal with, to give rise to, to utilize, to exploit, finite, firstly, secondly, in this respect.

EXERCISES

I. Join the word on the left with one on the right to make a two-word combination. Use each word once only.

1) important	a) affinity
2) become	b) reactions
3) charged	c) investigation
4) valuable	d) current
5) technological	e) rise
6) present	f) particles
7) scientific	g) civilization
8) chemical	h) needs

9) give	i) understanding
10) close	j) clear
11) modern	k) fields
12) societys	l) tools
13) electric	m) chemicals
14) increased	n) branch
15) industrial	o) emphasis

II. Answer the following questions:

1. What is electrochemistry? 2. Why is this branch of science of great importance? 3. What does electrochemistry deal with? 4. What can be said about the future of electrochemistry? 5. What methods have more advantages-electrochemical or conventional?

III. Find in the text sentences with verbals and verbal constructions, state their functions and translate the sentences into Russian.

IV. Read the following text at sight. Give a brief summary of the text.

Electrochemistry is the branch of chemistry which treats of the chemical changes that are due to electrical energy, and investigates the chemical changes by which electricity is produced. That electricity causes chemical changes may be illustrated by placing two platinum rods in a strong solution of common salt, and then connecting them with a battery or a dynamo. The current will then decompose the solution and the sodium will be set free at the negative electrode, while caustic soda will be formed as the sodium combines with the water; and at the same time the chlorine will escape in bubbles through the liquid being set free at the positive electrode. That chemical action produces electricity is demonstrated by placing a zinc bar in a solution of copper sulphate, the solution being separated by a porous partition, and as soon as the rods are connected by a wire a current of electricity will pass through the circuit.

Electrochemistry is employed in the manufacture of various chemical products, in extracting metals from their ores, and in electrotyping. It enters into the manufacture of carborundum chlorine, soda, and potassium chlorite. It is also vital in everyday life in the form of familiar dry cells and storage batteries.

Suggested Topics for Discussion

1. Speak on the subject of electrochemistry.

2. Speak on the contribution of electrochemistry to industry, technology and everyday life.

3. Speak on the advantages of electrochemical methods over conventional ones.

THE MYSTERIES OF SOLUTIONS

From the earliest days, scientists experimenting with chemistry have worked with solutions. The liquid they used for making a solution (usually water) they called *the solvent*. The chemical dissolved was called *the solute*.

When chemists began to use electricity as one of their tools, they discovered that different solutions behaved in different ways. The solution in water of a great number of chemicals – sugar among them – did not let electricity pass through.

In 1874 a Swedish scientist named Arrhenius developed a theory to explain the mysterious behavior of solutions. He was only 25 years old at that time. His idea was that when a chemical that conducts electricity is dissolved in water, each molecule is broken up – dissociated – into electrically charged atoms or groups of atoms. These atoms or groups of atoms Arrhenius called *ions* from a Greek word that means *to wander*. This new theory came to be called *the Arrhenius theory of ionization*.

When table salt (sodium chloride, NaCl), for instance, is dissolved in water, it ionizes into positively charged sodium ions (Na^+) and negatively charged chlorine ions (Cl^-) . These ions wander about in all directions until an electric current is applied to the solution. When that happens, the negative ions rush to the positive pole, the positive ions to the negative pole. It is the ions that conduct the current through the solution.

The reason that non-conductors do not conduct electricity is that they do not dissociate into ions.

The Arrhenius theory of ionization helped to explain a great number of things that had puzzled chemists. His theory has been modified somewhat over the years but in most respects holds true today.

Conversation on Chemistry (Dialogue) P a r t I

A l e c : Oh, Nick, here you are at last. I've been waiting for you all day. In the morning we had a long discussion on solutions.

N i c k : What's that you want to know about solutions?

A l e c : Well, a solution consists of two parts: the solvent and the solute.

N i c k : So, what's there to discuss?

A l e c : What is meant by the solvent?

N i c k : Don't you know such simple things?

A l e c : I hope I do. The liquid we use for making a solution is called the solvent. And the chemical dissolved is called the solute. Am I right? N i c k : You are quite right. That's exactly what your book on chemistry says.

A l e c : My schoolmate, Paul, says that we can make the solvent become the solute and vice versa. What do you think about it? Is it possible?

N i c k : Quite possible, Alec.

A l e c : How can that be?

N i c k : The matter is that the solute is the part present in the smaller amount, and the solvent is the substance present in the greater quantity. However, we can often reverse the relative amounts of the substances making solution.

A l e c : So, are both of us right, Paul and me?

N i c k : Surely, both of you are right.

Part II

A l e c : What's the difference between saturated and supersaturated solutions? I feel that though these names are similar, nevertheless there is some difference.

N i c k : Well, a concentrated solution is one that contains a large amount of dissolved substance.

A l e c : But I do know that.

N i c k : So, when a solvent has dissolved all the solute it can contain, the solution is called saturated.

A l e c : And what about a supersaturated solution?

N i c k : A supersaturated solution contains more solute than its solvent holds under normal condition.

A l e c : How can you prepare such a solution? I believe it is rather difficult.

N i c k : Nothing easier. You just dissolve a greater amount of solute than the solvent contains at ordinary temperatures. You can do that by heating it. When you cool it very slowly, you'll get a supersaturated solution.

Active Vocabulary

solution, solvent, solute, liquid, to dissolve, to behave, behavior, to develop, to conduct, conductor, to charge, ion, to ionize, to dissociate, to modify, in most respects, to hold true.

EXERCISES

I. Answer the following questions:

1. What is meant by a solvent and a solute? 2. What did chemists discover about solutions when they began to use electricity? 3. What solutions may be called electrolytes? 4. What theory did Arrhenius develop? 5. How old was Arrhenius at that time? 6. What happens to table salt when

it dissolves in water? 7. What ions are positively charged in this case? What ions are negatively charged? 8. What happens to these ions when an electric current is applied to the solution?

II. Choose the correct word from the list below:

1. A non-settling mixture of a solute in a solvent. 2. A liquid in which a solute is dissolved. 3. The number of grams of a solute needed to make a saturated solution in 100 grams of a solvent. 4. A substance that, when in solution or when melted, will conduct an electric current. 5. Breaking down a substance by passing an electric current through it.

(solubility, solution, electrolysis, solvent, electrolyte)

III. Read and translate the following text without a dictionary:

It often occurs that materials are found in nature in impure conditions. Thus, for example, the salt found in a number of mines contains other materials than sodium chloride, although the impurities may be present only as a few per cent. If the salt is dissolved to give a saturated solution, and the saturated solution is slowly evaporated, sodium chloride crystals form but many of the impurities remain in solution. Although the solution is saturated with respect to sodium chloride, it is not saturated with respect to the impurities. Thus by recrystallization an impure material can be worked up to a state of high purity. This is achieved the more readily the greater is the effect of temperature on the solubility of the compound in question.

IV. Read the text and answer the following questions:

1. What influences the rate of solution? 2. What is solubility? 3. What factors is solubility determined by? 4. What is a dilute solution? 5. What is a concentrated solution?

Solutions

We know a solution to be a uniform mixture of one substance in another. The material to be dissolved is the solute and the substance which does the dissolving is the solvent. The rate at which a substance may be dissolved can be controlled in several ways. The surface area, the agitation, and the temperature are found to have an effect on the rate of solution.

The ease with which a substance may be dissolved is known to be its solubility. The solubility of solid, liquid, or gaseous solutes is determined by a number of factors, such as the nature of the solvent, the nature of the solute, the temperature and the pressure. In a solution the solute cannot be separated from the solvent by filtration.

The concentration of the solute in a solution may vary from dilute (a small amount of the solute relative to the solvent) to concentrated (a large amount of the solute relative to the solvent).

The most common of the solvents is known to be water. Among the organic compounds such materials as alcohol and benzene are commonly used as solvents. Most organic compounds can be dissolved only in organic solvents.

Notes

1) agitation – волнение, колебание;

2) benzene – бензол;

3) rate – скорость.

IV. Translate the following sentences into Russian:

1. Water does dissolve most substances. 2. It is electrolytes that are good conductors. 3. Atoms are too small to be seen with unaided eye but they do exist. 4. It is the ions that conduct the current through a solution. 5. It was the Arrhenius theory of ionization that helped to explain a great number of things.

Suggested Topics for Discussion

- 1. Speak on the mysteries of solutions.
- 2. Speak on the Arrhenius theory of ionization.
- 3. Speak on saturated and supersaturated solutions.

DISSOCIATION OF WATER

The water molecule contains two covalent bonds, each linking the oxygen atom with one of the hydrogen atoms. The bonds are identical, and are not truly covalent, having a slight polarity which makes the hydrogen end of the bond positive and the oxygen end negative. Water is a very weak electrolyte and dissociates very slightly into a hydrogen ion and a hydroxyl ion:

$$H_2O \rightarrow H^+ + OH^-$$
.

Dissociation at one bond affects the pattern of the electrons, forming the other, in such a way that the second bond does not dissociate. Thus, water consists mainly of molecules with a few hydrogen and hydroxyl ions also present. The dissociation of water obeys the rules governing chemical equilibrium. The extent of the dissociation of water is very small, so that shifts from the equilibrium position producing large changes in the concentration of the ions, cause a negligible change in the concentration of undissociated water, which can be taken as a constant (Kw).

The equilibrium between undissociated water molecules and hydrogen and hydroxyl ions will exist in any aqueous solution, regardless of any other molecule or ionic species present. If a solution containing hydrogen ions is added to pure water, the dissociation of the water is reduced until the hydroxyl ion concentration becomes low enough for the above relationship to hold.

Active Vocabulary

dissociation, electrolyte, equilibrium, extent, pattern, mainly, shift, species, polarity, hydroxyl, slight, to affect, to cause, to change, to obey, to reduce.

EXERCISES

I. Answer the following questions:

1. What bonds does the water molecule contain? 2. What is the extent of the dissociation of water? 3. What can be taken as a constant? 4. What conditions is the dissociation of water reduced under?

II. Give Russian equivalents for:

a weak electrolyte, a hydroxyl ion, to obey the rules, to govern chemical equilibrium, the extent of dissociation, to take as a constant, to cause a change.

III. Form adverbs from the following adjectives and translate them:

true, slight, positive, negative, identical, pure, main, covalent, large.

IV. Translate the following sentences, paying attention to the words underlined:

1. The colour of this liquid changes <u>slightly</u> on heating.

2. Rain water is nearly <u>pure</u>.

3. A compound is <u>reduced</u> if hydrogen is added to it.

4. All samples of a substance possess the same properties and have the same composition <u>regardless</u> of their source.

5. Moisture <u>affects</u> many metals.

V. Compose sentences of your own with the following words:

electrolyte, to obey, to cause a change, polarity, pattern, species.

VI. Find attributive groups in the text and translate the sentences into Russian.

VII. Find in the text sentences with verbals and verbal constructions, state their functions and translate the sentence into Russian.

VIII. Read the text with a dictionary and answer the following questions:

1. What is called an anode? 2. What is a cathode? 3. What is called a cation? 4. What is an anion? 5. What is electrolytic conductance?

Electrolytic Conductance

If a pair of electrodes is placed in a solution of an electrolyte and a potential is applied across them, a current flows. The electrode connected to the positive terminal of the supply is called <u>an anode</u>, and the electrode connected to the negative terminal is called <u>a cathode</u>. Electrons leave the solution at the anode, and enter it at the cathode. The electrons themselves do not travel through the solution. The current through the solution is due to the movement of ions, the positively charged ions, or cations, moving towards the cathode, and the negatively charged ions, or anions, moving towards the anode.

Electrolyte solutions obey Ohm's law under certain circumstances. They are poor conductors compared with metals. The specific resistance of a 1% solution of common salt is about fifty million times that of copper. It is not usual to talk about the resistance of electrolytic solutions, but rather about their <u>conductance</u>. The specific conductance of a solution is defined as the reciprocal of resistance of part of the solution, 1 cm in length and 1 cm² in cross-section. The specific conductance of a solution increases with concentration because the number of ions increases, but the relationship is not simple. The decrease in the degree of dissociation which accompanies the increase in concentration, complicates the relationship in the case of weak electrolytes. In strong electrolytes the dissociation is complete.

IX. Read the following text and express the main idea of it:

Chemical Bonds

Chemical bonds between atoms result from the interaction of the electrons of the atoms concerned. The simplest example is probably the bonding between hydrogen atoms. The hydrogen atom has one unpaired electron, and a bond can form between two atoms due to interaction of their electrons. The result is a stable unit called <u>a molecule</u>, in which the two nuclei are held at a fixed separation, and the two electrons occupy a new orbital common to both. The change in electron pattern means a change in the chemical nature, and hydrogen atoms and hydrogen molecules react in very different ways. Two electrons occupying an orbital shared by two nuclei represent a single chemical bond.

Chlorine usually exists in molecular form, each molecule containing two atoms bonded by a single bond. The chlorine atom has one unpaired electron, and the bond is formed by two electrons occupying an orbital shared by the two nuclei. Under normal conditions nitrogen also exists in the form of diatomic molecules, but in this case there are three unpaired electrons, and three new orbitals are formed, each containing two electrons, one from each atom, and each shared by both nuclei.

In the examples given the influence of the electrons in the new orbitals is symmetrical about both nuclei. Such bonds are called <u>covalent</u>.

Chemical bonds can also be formed by the transfer of an electron from an orbital of one atom to the orbital of another. A simple example of this is the bonding between a lithium atom and a fluorine atom both of which have one unpaired electron. When the bond is formed the unpaired electron leaves the lithium atom to share the orbital of the unpaired electron of the fluorine atom. When a covalent bond is formed the result is a single new entity, the molecule in which the original atoms are held together by a common orbital.

This other type of bonding results in two new entities, oppositely charged due to the transfer of an electron and held together by electrostatic attraction. The new charged particles are called ions and retain the name of the atom from which they are derived. However, lithium ions and fluorine ions are very different in their chemical nature to the corresponding atoms. Bonds of this type are said to be <u>electrovalent</u>, or <u>ionic</u>. Covalent and ionic bonds can also exist in the same stable unit. But there are many bonds which are not ionic, but which are not truly covalent either. They are covalent when a new orbital common to both nuclei is occupied by two electrons, but the influence of the two electrons about the two nuclei is not symmetrical. This gives a charge separation, and a dipole results. The extent of the polarity in covalent bonds depends on the nature of the atoms concerned. In polyatomic molecules some bonds may be polar and other not.

X. Read the text at sight and entitle it.

Substances in which the bonding is ionic exist in the solid state as an arrangement of ions. These ions may be derived from a single atom, or from a number of atoms bonded together covalently. The ions are held together in a set pattern by electrostatic forces. The pattern is determined by the size of the ions and the magnitude of their charge. One of the simplest patterns is that of sodium chloride. When a covalent substance is heated the kinetic energy of the molecules is increased and at some temperature it becomes sufficient to overcome the inter-molecular forces. The solid melts to give a liquid which consists of a mass of freely moving ions. Thus, the melt of an ionic substance conducts electricity.

When dissolved in water, substances in which the bonding is covalent give a solution of molecules moving freely in the solvent. Glucose is an example of this. Substances in which the bonding is ionic give a solution consisting of ions moving freely in the solvent. The separation into ions can be easily demonstrated. One gram molecule of sodium nitrate and one gram molecule of potassium chloride are dissolved in one litre of water in one vessel, while one gram molecule of potassium nitrate and one gram molecule of sodium chloride are dissolved in one litre of water in another vessel. The two solutions are indistinguishable as they both contain sodium, potassium, nitrate and chloride ions in the same concentrations. Most ions in aqueous solutions are hydrated. They have molecules of water held to them by electrostatic forces. These act between the ion and the oppositely charged end of the water molecule, which is slightly polar. The number of associated water molecules varies from ion to ion. The agglomeration of ion and water molecules moves as an entity through the solution. Substances which give ions when dissolved in water are called <u>electrolytes</u>. Those which break down completely into ions are called <u>strong electrolytes</u>, and those which only partially dissociate are called <u>weak electrolytes</u>.

Notes

- 1) aqueous водный;
- 2) to derive получать, извлекать;
- 3) pattern модель, система, структура, пример;
- 4) indistinguishable неразличимый;
- 5) to hydrate гидротировать;
- 6) agglomeration скопление, агломерация;
- 7) entity сущность, что-либо реально существующее;
- 8) to dissociate диссоциировать.

Suggested Topics for Discussion

- 1. Speak on the dissociation of water.
- 2. Speak on the electrolytic conductance.
- 3. Speak on the ionization in aqueous solutions.

FARADAY, MICHAEL – ENGLISH PHYSICIST AND CHEMIST

Faraday (September 22, 1791 – August 25, 1867) was one of the ten children of a blacksmith. So, there was no question of an education for young Faraday and he was apprenticed to a bookbinder.

This, as it happened, was a stroke of luck, for he was exposed to books. Faraday's second stroke of luck was that his employer was sympathetic to the young man's desire for learning and allowed him to read books and attend scientific lectures.

In 1812 a customer gave Faraday tickets to attend the public lectures of Humphry Davy at the Royal Institution. Young Faraday took careful notes which he further elaborated with coloured diagrams and sent them to Sir Banks, president of the Royal Society, in the hope of getting a job that would bring him closer to science. When an opening as his assistant occurred, Davy offered the young man the job. Faraday took it in 1813, at the age of twenty-two, at a salary that was smaller than he had been earning as a bookbinder. Almost at once Davy left for his grand tour over Europe. He took Faraday with him as secretary and valet.

Faraday became director of the laboratory in 1825, and in 1833 he became professor of chemistry at the Royal Institution.

In chemistry Faraday made his first mark in 1823 when he devised methods for liquefying gases, such as carbon dioxide, hydrogen sulphide, hydrogen bromide and chloride, under pressure. He was the first to produce temperatures in the laboratory that were below the zero mark on the Fahrenheit scale. He may just be viewed as a pioneer in the modern branch of physics called cryogenics (the study of extreme cold).

In 1825 his greatest single contribution to organic chemistry occurred. He discovered benzene, a compound that was to play a key role in *Kekulé's* development of a means of representing molecular structure.

In addition Faraday carried on Davy's investigations in electrochemistry. Davy had liberated a number of new metals by passing an electric current through their molten compounds. Faraday called this process electrolysis. He named a compound or solution that could carry an electric current the electrolyte. All these names still exist unchanged and are used constantly in science.

In 1832 Faraday further reduced the matter of electrolysis to quantitative terms by announcing what are now called Faraday's laws of electrolysis.

Faraday's laws put electrochemistry on its modern basis. In his honour quantity of electricity required to liberate 23 grams of sodium, or 108 grams of silver, or 32 grams of copper (that is, to liberate an "equivalent weight" of an element) is called a faraday. And the unit of electrostatic capacitance is the farad, in his honour.

For some time Faraday was giving enormously popular lectures in science for the general public.

His theory of the lines of force (which he published in 1844) was not taken too seriously at first. However, when Maxwell came to tackle the matter of electromagnetism with precise mathematical tools, he was to end with the same picture, mathematically phrased, that Faraday had drawn in simple words.

In later years Faraday made more discoveries in connection with electromagnetism and its interaction with light.

When he was eventually offered the presidency of the Royal Society, he refused and he also declined an offer of knighthood. He was intent on being plain Michael Faraday.

Active Vocabulary

a blacksmith – кузнец, to apprentice – отдавать в учение, a bookbinder – переплетчик, a stroke of luck – удача, sympathetic – полный сочувствия, благожелательный, a valet – камердинер, лакей, cryogenics – наука о низких температурах, to liberate – освобождать, выделить, in one's honour – в чью-либо честь, to decline – отклонять, отказываться, knighthood – рыцарское звание, дворянство, to view – рассматривать, оценивать.

EXERCISES

I. Answer the following questions:

1. When and where was Michael Faraday born? 2. What was his father? 3. Was Faraday apprenticed to a bookbinder or to a butcher? 4. Why did he attend Humphry Davy's lectures at the Royal Institution? 5. When did he make his first mark in chemistry? 6. He became a professor of chemistry in 1833, didn't he? 7. What can be said about his first discoveries? 8. Was he a pioneer in the branch of physics called cryogenics? 9. What was Faraday's single contribution to organic chemistry? 10. What can be said about his contribution to electrochemistry? 11. What is called a faraday? 12. Did Faraday express the matter of electromagnetism in simple words or with precise mathematical phrases? 13. It is interesting to know if Faraday was offered the presidency of the Royal Society? 14.Was the great scientist a modest person?

II. Translate the following sentences, containing additional information about the life of Michael Faraday.

1. Faraday's father could feed his family with difficulty, and could not even dream of an education for his boy.

2. Some of the scientific papers which passed through Michael's hands aroused his interest in science.

3. The more he studied, the more interested he became.

4. When Faraday learnt more about electricity, he grew discontented with his work at the bookbinder's shop.

5. Humphry Davy asked Faraday to come to see him, and offered him an opportunity to do scientific research.

6. In Europe, Faraday met, among other people, Volta and Ampere.

7. Faraday's scientific interests were varied. He made a new kind of steel and a new kind of glass. He studied flying.

8. He often worked fourteen hours a day.

9. During his lifetime Faraday made more than two thousand different experiments and countless valuable discoveries in chemistry and physics.

III. Read the text and say a few words about Davy's contribution to chemistry.

Humphry Davy

Humphry Davy was born in England in 1778 and died in 1829. He studied chemistry and became an assistant in the Medical Institution in Bristol. His experiments were largely in gases, especially in pure nitrous oxide, or "laughing gas". It led him to the appointment as professor of chemistry at the Royal Institution of London, where his chief interest was electrochemistry. He also began researches in agricultural chemistry. Humphry Davy succeeded in preparing potassium and sodium by the process of electrolysis in 1807. Later he determined the nature of chlorine and discovered calcium, strontium, boron, and barium. He traveled much in Europe where he received many honours. He returned to England in 1815 and later investigated the nature of firedamp, the explosion of which had caused much damage in mines. These investigations led him to his invention of the safety lamp (1815). In 1820 he became President of the Royal Society. His writings include "Elements of Agricultural Chemistry", "On Some Chemical Agencies of Electricity", and "Elements of Chemical Philosophy".

Notes

1) firedamp – рудничный газ;

2) explosion – взрыв;

3) damage – повреждение, разрушение;

4) safety lamp – рудничная лампа;

5) honours – почести.

IV. Read the text at sight and entitle it.

William Whewell, a philosopher, mineralogist and historian of architecture was the man who originally devised such English words as "scientist", "physicist" and many other scientific terms. One of the people who turned to Whewell for advice was Michael Faraday. He wanted names by which he could refer to things without involving any theory of the nature of electricity. The result was that Whewell coined the two words "anode" and "cathode", for the places where an electric current enters and leaves a conducting fluid. They are now in universal use in electrical and electronic engineering.

In suggesting the words "anode" and "cathode", Whewell emphasized that their origins are genuine Greek words and not compounds coined for the purpose. He was not against inventing new words when necessary, but preferred to make use of old ones wherever that was possible. It was one of the seventeen principles for coining new terms which Whewell down in his book "Philosophy of the Inductive Sciences". Thus "scientist" was derived from "science" and "physicist" from "physics". Before Whewell invented the words all scientists have been called "natural philosophers". Other Whewell words in common use are "ion", "paramagnetic" and "diamagnetic".

Suggested Topics for Discussion

- 1. Speak on the life and work of M. Faraday.
- 2. Speak on H. Davy and his role in M. Faraday's life.
- 3. Speak on the farther of English scientific terms.

ELECTROLYSIS

When a current is passed through a solution of an electrolyte the ions move towards the electrodes. When they arrive they gain or lose electrons and a chemical change occurs. The chemical change brought by passing a current through an electrode is called electrolysis. Much of the early work in the field was carried out by Michael Faraday. He showed that the extent of the reaction was proportional to the amount of electricity passed. He also showed that 96,500 coulombs would liberate one gram equivalent (the molecular weight divided by the charge on the corresponding ion) of any substance from solution. This amount of electricity is known as the *faraday*. These two results are known as Faraday's laws of electrolysis. They follow from the fact that all ions carry small whole numbers of the basic unit of electricity, $1,6 \cdot 10^{-19}$ coulombs. When ions reach the relevant electrode they may be discharged, losing or gaining electrons.

In some cases the resultant neutral particle is stable. This is the case with metal ions which are converted into atoms. In other cases, even when the discharged ion becomes an atom, it is not stable and reacts with other similar atoms to give molecules, e. g.

 $H^+ + e \rightarrow H$ followed by $H + H \rightarrow H_2$.

In many cases the ion is not based on one atom, but on a number of covalently bonded atoms, and chemical reactions occur between the resultant particles on discharge, e. g.

$$OH^- \rightarrow OH + e, 2OH \rightarrow H_2O + O, O + O \rightarrow O_2.$$

The reactions of the discharged ions may involve the material of the electrode, or other substances present. In some cases the ions are not discharged on the arrival at the electrode. Instead, ions of the opposite

charge enter the solution from the electrode. This can occur if a solution of a metal salt is electrolysed between electrodes of the metal. Metal ions are discharged at one electrode, while metal goes into solution as ions at the other, instead of the other ionic species being discharged.

The chemical changes which occur at the electrodes lead to concentration changes in the solution. There is a steady change in the overall concentration if the ionic species are discharged. There are also changes in the local concentrations in the region of the electrodes. For a given amount of electricity passing through the solution, the number of electrons taken up by the positive ions at the cathode, must equal the number of electrons given up by the negative ions at the anode. Consider the simple idealised case of a solution which contains only two types of ion, both positive and negative ions carrying a single charge, both travelling at the same speed through the solution, and both being discharged on the arrival at the electrode. If *n* electrons enter the solution at the cathode, *n* positive ions will be discharged. The same number of electrons must leave the solution at the anode, and *n* negative ions must also be discharged. The passage of the current through the solutions involves the movement of *n* charged particles. As the ions move at the same speed, this will involve a movement of n/2 positive ions in one direction, and n/2 negative ions in the other direction. In the vicinity of the cathode the following changes occur:

n positive ions out discharge

n/2 positive ions in

n/2 negative ions out \int current carrying

The net result is a reduction in the number of both ions by n/2. This is a reduction in the concentration of the electrolyte. A similar reduction in the concentration of the electrolyte occurs in the vicinity of the anode. At each electrode n ions are discharged, but, only n/2 arrive as a result of current carrying. If a steady current is flowing the process is continuous. Initially, the concentration of the electrolyte in the vicinities of both electrodes is reduced, but then ions of both types diffuse into these regions under the influence of the concentration gradients. This involves no charge transfer. A steady state is reached when the number of ions reaching the electrode by both mechanisms is equal to the number discharged.

If the electrolyte had been a metal salt, and the electrodes had been of the same metal, negative ions arriving at the anode would not be discharged by giving up their electrons. Instead, the metal would ionise, leaving electrons on the metal electrode. This would produce a local increase in concentration of the electrolyte, and ions of both types would then diffuse away from the electrode.

Active Vocabulary

a coulomb – кулон, whole – целый, единый, resultant – проистекающий из, stable – устойчивый, постоянный, to discharge – разряжать, выделять, освобождать, electrode – электрод, overall – общий, окончательный, суммарный, net result – окончательный результат, reduction – понижение, сокращение, восстановление, in the vicinity – около, transfer – перенос, to diffuse – диспергировать, распространять(ся).

EXERCISES

I. Answer the following questions:

1. What is called electrolysis? 2. What is it based on? 3. What is known as Faraday's laws of electrolysis? 4. Under what conditions is there a steady change in the overall concentration? 5. Are there changes in the local concentrations? 6. What changes occur in the vicinity of the cathode?

II. Find antonyms in a) and b) groups and arrange them in pairs:

a) to lose, to arrive, small, absent, overall, increase;

b) to leave, local, to gain, large, present, decrease.

III. Give nouns corresponding to the following verbs:

to arrive, to electrolyse, to pass, to convert, to move, to reduce, to consider.

IV. Compose sentences of your own with the following words:

instead, resultant, relevant, steady, to involve, initially.

V. Translate paying attention to the words underlined:

1. The mass of a substance <u>liberated</u> at the electrode during electrolysis is <u>proportional</u> to the quantity of electricity passed through the solution.

2. The mass <u>liberated</u> by a given quantity of electricity <u>is proportional</u> to the atomic weight of the element <u>liberated</u> and inversely <u>proportional</u> to the valence of the element <u>liberated</u>.

VI. Find in the text sentences with verbals and verbal constructions, state their functions and translate the sentences.

VII. Translate the following text with a dictionary:

Laws of Electrolysis

Faraday investigated the relation between the quantity of electricity passing through a voltameter and the masses of the products liberated. He first established that the current is of the same magnitude everywhere in the same circuit.

<u>Faraday's first law</u>. The first law proper gives the relation between the mass of any element or radical liberated and the quantity of electricity passed through the electrolyte. It is as follows: The mass of any element or radical liberated is directly proportional to the quantity of electricity

passed. In Faraday's own words: "The quantity decomposed is exactly proportionate to the quantity of electricity which has passed".

A current measurer was at the time badly needed. Faraday suggested that this first law could be a basis for measurement. The ampere was subsequently defined as the current which will deposit 1,118 milligrams of silver per second from a solution of silver nitrate.

<u>Faraday's second law</u> deals with the masses of different elements or radicals liberated by the same quantity of electricity. In the same circuit, the masses of hydrogen, silver and copper liberated or deposited from acidulated water, silver nitrate and copper sulphate, respectively, are different.

Faraday proved that the masses of products liberated by the quantity of electricity are proportional to their chemical equivalents.

This is Faraday's second law.

VIII. Read the following text, look at the scheme and try to retell the text in brief:

Faraday's Laws

As it is known, current flow in metals is due to electrons, and in electrolytes usually to ions. If, therefore, metallic and electrolytic conductors are in the circuit, at one phase boundary between metal and solution electrons must be produced and at the other they must be taken up. Acceptance of electrons, e. g., as in $Ag^+ + e \rightarrow Ag$, or $Cl + e \rightarrow Cl^-$ implies reduction, whereas donation of electrons implies oxidation, so that the passage of a current across phase boundaries is always associated with oxidation-reduction reactions. If these reactions are produced by an externally applied potential electrolysis is said to occur, and if the reaction takes place in the reverse direction spontaneously, an electric current is produced and the system is termed a galvanic cell. The relation between the quantity of electricity passed and the quantity of chemical substance used up was studied by Faraday. His numerous and careful investigations led to the two laws named after him. The first of these is:

The mass of a substance electrolytically produced is proportional to the quantity of electricity passed. Faraday based this law upon the following experiment (see Fig. I). A current is passed through three electrolytic cells filled with dilute H_2SO_4 , of which II and III are in parallel and both are in series with I. Hydrogen and oxygen are evolved, collected separately and volumetrically determined. It is found that in I exactly as much hydrogen and oxygen is evolved as in II and III together and this result is independent of the applied potential (so long as this is great enough to cause electrolysis) of the size of the electrodes (and hence of the current density) and of the concentration of sulphuric acid.



Fig. I. Examination of Faraday's Laws

IX. Read the text at sight and entitle it.

A considerable share of the power generated by electric stations is supplied to the chemical industry and to metallurgy.

The most active metals (such as the alkali metals) and the most active non-metals (the halogens) occur in nature only in the form of compounds that contain the metals in the form of positively charged ions and the nonmetals in the form of negatively charged ones. To isolate the metal from such compounds it is necessary to restore to its ions the electrons they lack; to isolate the non-metals, it is necessary to detach from their ions their excess electrons. For example:

$$Na^{+} + e = Na^{0};$$

 $2Cl^{-} - 2e = 2Cl^{0} = Cl_{2}^{0}.$

This can be affected by electrolysis. Indeed, electrolysis is the only possible method of preparing free fluorine and the only expedient method of preparing the metals situated at the head of the electromotive series. Electrolysis is therefore employed in industry to prepare the most active metals, including aluminium, as well as free chlorine and fluorine.

Electrolysis is also employed for electrolytic nickel- and chromiumplating. This is accomplished by placing articles in baths with solutions of suitable compounds of nickel or chromium, connecting the articles to the negative terminal of a source of a direct current, and passing the current through them for the time needed to coat the articles with a layer of nickel or chromium of required thickness. Such treatment not only gives the articles an attractive appearance (a dazzling surface that is slightly yellowtinged in nickel-plated and slightly bluish in chromium-plated articles), but protects them from chemical attack (corrosion).

By means of electrolysis it is possible to deposit metal on the surface of embossed articles and then, by removing the deposited layer of metal, to obtain facsimiles in relief of the articles. This technique of obtaining facsimiles in relief by means of electrolysis is called galvanoplastics, or electrotyping. It was invented by the outstanding Russian scientist B. Yakobi.

Suggested Topics for Discussion

- 1. Speak on electrolysis.
- 2. Speak on the laws of electrolysis.
- 3. Speak on practical applications of electrolysis.

THE ELECTROCHEMICAL CELL

Neither pure water nor ionic crystals (copper sulphate, for example) are electrical conductors. However, when mingled to form a solution, they become conductive to an extent determined largely by concentration. The solid conductors by which electric current enters and leaves the solution are termed *electrodes*. The ionic substance which imparts conductivity to water is called *an electrolyte*, a term also being used to refer to the solutions themselves.

The basic difference between conduction in metals and in electrolytes is that in metals electrons move independently, whereas in solutions they move only as constituent parts of ions or molecules. An electron leaving a metallic conductor to enter a solution must be associated with some chemical species. Such association (addition) is, by definition, <u>chemical reduction</u> and occurs whenever current flows between electrodes.

An electron leaving a solution disassociates from a chemical species. This process, again by definition, is <u>oxidation</u>. The electrode at which reduction proceeds is called the cathode, that at which oxidation occurs, the anode. The chemical changes at the electrodes are termed *electrolysis* (decomposition by electricity). Anode, cathode, solution and container make up an <u>electrochemical cell</u>.

When current is supplied to the cell from an external source, it is said to be an <u>electrolytic</u> cell; if current is drawn <u>from</u> the cell, it is called a <u>voltaic</u> or <u>galvanic</u> cell. Electrolysis occurs in both types. It is customary to call the anode positive in an electrolytic cell, but negative in a galvanic cell; the cathode, of course, has opposite designations. A positively charged ion is termed a <u>cation</u>, it is attracted to the cathode in an electrolytic cell. A negatively charged ion is an <u>anion</u>. These terms apply in both electrolytic and galvanic cells, notwithstanding the reversed sign designations of the electrodes.

Active Vocabulary

to mingle – смешивать(ся), to determine – определять, устанавливать, to impart – наделять, делиться, передавать, сообщать, aconstituent – составная часть, элемент, a species – род, вид, разновидность, by definition – по определению, decomposition – разложение, распад, a cell – электролитическая ванна, ячейка, элемент, voltaic – гальванический, customary – обычный,

привычный, designation – обозначение, название, знак, notwithstanding – несмотря на, вопреки, anion – анион, cation – катион.

EXERCISES

I. Answer the following questions:

1. What is called an electrode? 2. What is called an electrolyte? 3. What is chemical reduction? 4. What is called the cathode? 5. What is called the anode? 6. What makes up an electrochemical cell? 7. What is the difference between electrolytic cells and galvanic ones? 8. What is termed an "anion"? 9. What is termed a "cation"?

II. Find synonyms to the words in a) and b) groups and arrange them in pairs:

a) to occur, to mix, mainly, to call, to continue;

b) to mingle, to proceed, largely, to take place, to term.

III. Make up sentences of your own with the following words and word combinations:

chemical reduction, a voltaic cell, a cation, an anion, whenever, reversed, by definition.

IV. Translate paying attention to the words underlined:

1. The process oxygen takes part in is known as oxidation.

2. As long as water evaporates in an open vessel, water vapour <u>mingles</u> with the atmosphere because of diffusion.

3. Newton first explained why all objects on the Earth <u>attracted</u> one another.

4. Magnesium is of great value as <u>a constituent</u> of light alloys.

5. The word "crystal" was first applied to ice and quartz.

V. Find in the text multi-component attributive groups and translate them. Pay attention to the parts of speech which compose these groups.

The models are: Noun + Noun (copper sulphate) and Adj + Noun (basic differences), etc.

What model is the most frequent one in the above text?

VI. Read the text with a dictionary. Remember that your study objective is to draw a galvanic cell, labeling the anode, the cathode, the charges on the electrodes, and the directions of electron and ion flow.

The Galvanic Cell

Here we discuss oxidation-reduction reactions. In many of these reactions, electrons are transferred from the reducing agent to the oxidizing agent.

 $Cu(s) + 2Ag(aq) \rightarrow Cu(aq) + 2Ag(s).$

reducing agent oxidizing agent

Copper metal is the reducing agent because it supplies electrons to the silver ion. The silver ion is the oxidizing agent because it removes electrons from copper.

It is possible to build a device in which electrons must move through an external electrical circuit, rather than transfer directly from an atom of the reducing agent to an atom of the oxidizing agent. Such a device which utilizes a spontaneous red/ox reaction, is called a galvanic or voltaic cell. The design of a galvanic cell is such that the reactants are prevented from direct contact with each other. The oxidation half-reaction occurs at an electrode called the anode, and the reduction half-reaction occurs at an electrode called the cathode.

Ex. 1. In your diagram you should show a copper-silver galvanic cell. The anode is a bar of copper metal that is partially immersed in a solution of $CuSO_4$. The cathode is a small bar of silver that is partially immersed in a solution of AgNO₃. The reducing agent, Cu metal, does not come into direct contact with the oxidizing agent, Ag ion. The electrons given up by Cu atoms must travel through the outer circuit to the Ag electrode, where Ag ions from the solution are reduced. As the reaction proceeds, the copper electrode loses mass and the silver electrode gains mass.

While electrons travel through the outer circuit from Cu to Ag (from the anode to the cathode), negative ions move through a porous barrier or a "salt bridge" from the AgNO₃ solution into the CuSO₄. This motion resupplies negative charge to the anode compartment, and maintains electrical neutrality in the solutions surrounding the electrodes. An electrical current will flow until either the Cu metal or the Ag⁺ ions are used up.

The fact that electrons flow from the anode to the cathode means that a voltage difference exists between the two electrodes. This voltage difference depends on the nature of the species involved in the half-reactions. The voltage measured across the two electrodes is called the electromotive force, or cell *emf*. The cell *emf* is represented by the symbol ε and is mea-sured in units of volts.

Suggested Topics for Discussion

- 1. Speak on the electrochemical cell.
- 2. Speak on electrolytic cells.
- 3. Speak on galvanic cells.

ELECTROMETALLURGY

Electrometallurgy is the science and technology of metallurgical operations conducted by electrochemical means; specifically, their use of electrolytic processes in the extraction and refining of metals and in electroplating; the term also encompasses the use of electric arc, resistance and induction furnaces.

Sir H. Davy first isolated the alkaline metals by electrolysis of fused salts. Davy's brilliant student, Michael Faraday succeeded in setting down the theoretical relations between equivalents of electricity and equivalents of mass in electrolytic cells. Other pioneers in the field included Johann W. Hittorf, Svante Arrhenius and Charles M. Hall. The early studies of electrolytes were aimed at the structure and degree of dissociation of ionic solutions, types of electrical conductivity and the separation of elements from aqueous and fused salt electrolytes, later studies of thermodynamics established the energy relations involved in electrochemical reactions.

Electrometallurgy is concerned with mechanisms of electrical conduction, rates of ion migration, galvanic and electrolytic cells, thermodynamics of cells and polarization. Electrical conductivity may be classified broadly into two main categories – electronic and ionic. Electronic conduction occurs by the passage of electrons while ionic conduction occurs by the migration of ions. In a closed electronic circuit no net mass transfer accompanies the flow of electrons along the current path; however, a mass flow does take place within electrolytic circuits, although no net mass flow occurs in the external circuit. This observation can be accounted for by the migration of relatively heavy ions of different masses in the electrolyte, in comparison with the motion of light mobile electrons in the external circuit. Faraday's laws govern the amounts of the electrode reactions.

Active Vocabulary

electrometallurgy, extraction, refining, encompass, induction, to set down, to aim at, thermodynamics, to migrate, broadly, comparison, to govern, mobile.

EXERCISES

I. Answer the following questions:

1. What is electrometallurgy? 2. Who was the first to isolate alkaline metals by electrolysis? 3. What other pioneers in the field of electrometallurgy do you know? 4. What were the early studies of electrolytes aimed at? 5. What did later studies of thermodynamics establish? 6. What is electrometallurgy concerned with?

II. Give Russian equivalents for:

an electric arc, an induction furnace, later studies, energy relations, ion migration, thermodynamics of cells, two main categories, a closed electronic

circuit, net mass transfer, a current path, net mass flow, to account for, in comparison with, an external circuit.

III. Form adverbs from the following adjectives and translate them: specific, brilliant, theoretical, broad, relative, heavy.

IV. Read the text with a dictionary and answer the following questions:

1. What is electrorefining? 2. Is electrorefining the most economical method? 3. In what cases is electrorefining used?

Electrorefining

This is a purification process in which the impure metal is made the anode (positive electrode) in a solution of a salt of the metal being refined. The pure metal deposits at the cathode during electrolysis.

Electrorefining has proved to be the most economical method for securing the high purity required for many commercial nonferrous metals. This process was applied to copper in the latter part of the nineteenth century, or as soon as the electric generator was invented. Electrorefined copper is an important material in the electrical industry since minor quantities of some impurities will lower the electrical conductivity of copper very markedly, for example, 0.01% arsenic in copper lowers the conductivity by 3%. Further, silver and gold are common constituents of copper ore and follow along with copper through all the pyrometallurgical steps. The removal of the silver and the gold from the copper is carried out in the electrolytic refining step. Thus, the refining process ensures that the metal will meet the specification of the purchaser and permits the recovery of precious metal impurities.

Impure metal slabs are cast in varying sizes and shapes, depending upon the particular metal being refined, to permit vertical hanging in the refining cells. In this case of copper, the anode is approximately 36 in. by 36 in. by $1^{3}/_{4}$ in., cast with lugs to support the anode front the walls of the cell or from the bus bars. These anodes weigh about 650–700 lb each. The cathodes are made of pure copper sheet, usually deposited on a smooth starting blank, stripped from the blank, and then suspended from a copper bar. The electrode spacing from anode center to cathode center is approximately 4 in. A current of about 15–25 amp/ft² of electrode surface is passed. This will consume about 20–30 lb of anode per day depending on current density, current efficiency, and the amount of slime formed.

The solution employed contains a salt of the metal being refined. In this case of copper a solution containing about 45g/liter of copper as copper sulfate with approximately 200 g/liter of sulfuric acid, is used. A temperature of 55–60°C is maintained to lower the resistance, and the electrolyte is

circulated through the cell. The size of the cell is again dependent upon the metal being refined.

V. Write the translation of the following text:

Electrometallurgical Operations

One of the earliest commercial processes in electrochemistry was that devised by E. H. and A. H. Cowles in 1884. A mixture of about two parts of alumina, one or two parts of granulated copper, and one or two parts of carbon was introduced in a brick-work chamber. Bundles of carbon rods inserted at the ends formed the electrodes between which a current of 3,000 amperes at 50 volts was maintained. At a very high temperature the alumina was reduced ($Al_2O_3 + 3C = 2Al + 3CO$) and the resulting aluminium combined the copper to form aluminium bronze. This was the forerunner of the various types of electrothermal operation described in the following paragraphs.

In general, electrometallurgical operations may be purely electrochemical, or a combination of both, depending on whether the process in question utilizes only the heat generated by the electrical energy, the chemical decomposing power of a direct current, or both together. Electrochemical processes are mostly used-for the direct reduction of a metal from its ores, for melting, or for refining metal in liquid form Since heat alone is required, alternating current is almost invariably used, as it is cheaper to produce and distribute. In any process where the chemical action of the current is required direct current must be used for the deposition of metals after extraction from their ores by solution, in electrolytic refining, and in several cases of the electrolysis of a fused salt.

Commercially, the most extensive applications of electrothermal processes are in the refining of steel and the production of ferroalloys; of the electrolytic processes the most important are the recovery of copper and zinc from leached ores, and the electrolytic refining of copper and lead although there are many other of lesser importance.

Suggested Topics for Discussion

- 1. Speak on electrometallurgy.
- 2. Speak on electrorefining.

ELECTRODEPOSITIOH

The most important type of chemical reaction brought about by the passage of electric current is the deposition of a metal at a cathode from a

solution of its ions. Electroplating of many metals, such as silver, cadmium, nickel and chromium is used for protective and decorative coatings. Electroforming is a variety of electrodeposition in which an article to be represented is rendered conductive by spraying a thin metallic coating, then electroplated with a metallic deposit that is stripped from its substrate and filled with backing to reproduce the original article. Electrowinning is used for the commercial production of active metals, such as aluminum, magnesium, and sodium, from molten salts and others, such as copper, manganese and antimony, from aqueous solutions. Electrofining is commonly used to purify metals such as silver, lead, and copper. The impure metal is used as the anode, and purified metal is deposited at the cathode.

Active Vocabulary

an article, deposition, electroplating, coating, electroforming, substrate, backing, electrowinning, electrorefining, to bring about, to render, to spray, to strip, to fill, to reproduce, to purify, impure, decorative, protective.

EXERCISES

I. Answer the following questions:

1. What type of chemical reaction brought about by the passage of electric current is the most important? 2. What is electroplating used for? 3. What is electroforming? 4. What is electrowinning used for? 5. What is electrofining?

II. Give Russian equivalents for:

protective and decorative coatings, the original article, impure metals, electroplating, electrodeposition, electrowinning, electroforming, electro-refining, molten salts, antimony, to purify metals, purified metals.

III. Translate the following words of the same root:

1) to decorate, decoration, decorative; 2) to conduct, conductance, conduction, conductivity, conductive; 3) to produce, production, productivity, product; 4) to purify, pure, purity, purification.

IV. Make up sentences of your own with the following words and word combinations:

to bring about, to spray a coating, to fill, substrate, to reproduce, to back.

V. Find the line in which there are only nouns:

1) important, article, reproduce, substrate;

2) protective, production, represent, variety;

3) fill, aluminium, purify, active;

4) deposit, lead, coating, manganese.

VI. Translate into Russian paying attention to the words underlined:

Chemical element, Cr, atomic number 24, atomic weight 51.996, a silver-white metal that is hard and brittle as <u>commonly</u> encountered. How-ever, the bulk metal is relatively soft and ductile when unstressed and either effectively scavenged or extremely <u>pure</u>. Chromium was discovered in 1798 by N. L. Vauquelin. Its chief uses are production of noncorrosive, high-strength, heat-resistant characteristics in alloys and as an <u>electroplated coating</u>. The most important mineral occurrence of chromium is in chromite, FeOCr₂O₃, which is never found <u>pure</u>. It is a dark-brown to jet-black octahedral mineral containing interstitial impurities, mostly magnesium silicates and other silicates.

VII. Translate into Russian:

Anodizing

In anodizing, a process related to plating, an oxide is deposited on a metal which is the anode in a suitable solution. The process is primarily used with aluminium, but it can be applied to beryllium, magnesium, tantalum, an titanium. Relatively thick oxide deposits can be produced, even though they are electrically insulating. The presence of small pores through which the solution can reach the metal surface permits the continuation of the reaction. The electrical current is carried by the electrolyte in the pores. Solution for anodizing aluminium generally contains either chromic or sulfuric acid. After anodizing the pore should be-sealed, to improve protection of the substrate, by a hot water or steam treatment which causes hydration and a resulting volume expansion of the oxide. Coloured coatings can be produced by incorporating dyes.

Suggested Topics for Discussion

- 1. Speak on electrodeposition.
- 2. Speak on anodizing.

ELECTROWINNING

This process is an electrochemical reduction of a metallic compound to the metal. In this process the ore or a roasted concentrate is leached with an acid solution. The solution is then circulated through a cell in which there are suspended insoluble anodes and cathodes. High purity metal can be obtained by this method, provided the proper solution control is maintained. In the case of zinc winning, the electrolyte is a sulfuric acid zinc sulfate solution in a lead-lined concrete tank. The anodes are lead containing small amounts of silver, usually have about 9 ft² of submerged surface, and weigh about 100 lb

each. Aluminium sheet is usually the cathode material. The accumulated zinc is stripped from the cathode sheet approximately once a day.

A calcine which is soluble in sulfuric acid is produced by roasting an ore of the metal. Impurities originally present on the ore that are soluble in sulfuric acid are removed in two steps. The first involves increasing the pH (lowering the acidity) of the leach solution to the point where the ferric hydroxide precipitates. The precipitate has a strong tendency to adsorb and coprecipitate many impurities. The electrolyte is next treated with zinc dust, and metals more noble than zinc are galvanically replaced, that is, precipitated, from the solution. It is imperative that all metals with low hydrogen overvoltage be removed from the solution before the electrolyte is introduced into the cell. Traces of germanium will result in practically zero cathode current efficiency. Current efficiency is the ratio of the amount of electricity (coulombs) theoretically required to yield a given quantity of metal to the amount actually consumed. Many other impurities act the same way, but not all of them as markedly as germanium. Since the reduction potential of zinc is far more cathodic than that of hydrogen ion, the cathodic deposition of zinc depends upon maintaining a high hydrogen overvoltage. Metals of low hydrogen overvoltage remaining in the electrolyte will deposit if they are more noble than zinc, forming centers for hydrogen evolution on the cathode, and, thereby, reducing the current efficiency for zinc deposition. The presence of these more noble metals on the cathode also promotes the dissolution of zinc already deposited by setting up a local galvanic cell, the cathodic potential being insufficient to yield complete cathodic protection; this again reduces the current efficiency. Thus, in practice, great care is exercised to see that the solutions are purified extensively. These difficulties are not nearly as serious in the case of electrowinning of more noble metals such as copper.

Active Vocabulary

electrowinning, to roast, to suspend, concrete, to set up, to adsorb, imperative, overvoltage, markedly, noble.

EXERCISES

I. Answer the following questions:

1 What is electrowinning? 2. What kind of metal can be obtained by this method? 3. How often is the accumulated zinc stripped from the cathode sheet? 4. What is the method of removing impurities present on the ore? 5. Is it imperative that all metals with low hydrogen overvoltage be removed from the solution before the electrolyte is introduced into the cell? 6 What is current efficiency?

II. Give Russian equivalents for:

a roasted concentrate, the proper solution control, in the case of, a lead-lined concrete tank, submerged surface, once a day, in two steps, leach solutions, a strong tendency, low hydrogen overvoltage, current efficiency, hydrogen evolution, noble metals, to set up a cell, to yield protection.

III. Find in the text sentences with the Gerund, state their functions and translate the sentences into Russian.

IV. Read the text with a dictionary and answer the following questions:

1. What is the method of obtaining fluorine, aluminium, sodium and other metals? 2. Why should raw materials be purified before addition to fused salt cells? 3. What keeps the products H_2 and F_2 separated? 4. Where is aluminium produced? 5. What does the Don process use for making magnesium?

Fluorine, aluminium, magnesium, sodium, lithium, beryllium, calcium, cerium are obtained by electrolysis of fused salts because water interferes with the desired reaction. Raw materials must all be purified before addition to fused salt cells, because purification of the electrolyte is not economical as in aqueous electrolytes.

Fluorine is produced by electrolysis of 40% in HF in KF between carbon anodes and steel cathodes at 100–110°C. A diaphragm of Monel screen keeps the products H_2 and F_2 separated. Dry HP gas is bubbled continuously into the electrolyte.

Aluminium is produced in carbon-lined steel pots containing an electrolyte of alumina dissolved in anode at 950–1000°C. The bottom of the pot is the cathode. It is siphoned out periodically. Oxygen released at the anode reacts with the carbon to form carbon monoxide.

Magnesium is produced by electrolysis of fused 25% MgCl₂, 75% NaCl at around 700°C. The Don process for making magnesium from sea water uses cell feed material approximating MgCl₂ \cdot 2H₂O which is fed around the graphite anodes where dehydration occurs. Gas from the anode compartment is wet chlorine, air and hydrogen chloride which is used to make fresh magnesium chloride from magnesium hydroxide. Magnesium metal is deposited on steel cathodes which direct the metal to a collecting zone. The cell is a cast-steel pot in a furnace setting, European cells use molten anhydrous magnesium chloride feed. They have brick-lined steel bodies with graphite anodes. Concentrated chlorine from the cells chlorinates MgO and coke in electrically heated shaft furnaces, from which molten MgCl₂ is tapped periodically to feed the cells. Molten magnesium is ladled from the cells and cast into molds protected by an atmosphere of SO₂.

Sodium was once made by electrolysis of fused NaOH. But since 1929 it has been made by electrolysis of NaCl in the Downs cells. The electrolyte is sodium chloride-calcium chloride eutectic (33.2% NaCl) at 600°C. The cell consists of a brick-lined steel vessel. Graphite anodes project upward from the bottom. The cathode is made of steel cylinders concentric with the anodes and supported from iron arms extending through the sides of the cell. A diaphragm in the form of steel screen directs the sodium into an inverted trough leading to a pipe which conducts it to a collecting tank above the cell. Chlorine is collected in an inverted cone over the anode. Pure, dry salt is fed to the cell.

Lithium is made in a cell similar to the Downs sodium cell except that the electrolyte is 60% LiCl, 40% KC1 at 450–500°C.

Suggested Topics for Discussion

1. Speak on electrowinning.

2. Speak on the production of fluorine, aluminium, magnesium and sodium.

ELECTROPLATING OF METALS

The process of electrodepositing metallic coatings is used to alter the existing surface properties or the dimensions of an object. Electroplated coatings are applied for decorative purposes, to improve resistance to corrosion or abrasion, or to impart desirable electrical or magnetic properties. Plating is also used to increase the dimensions of worn or undersized parts. An example of a decorative coating is that of nickel and chromium on automobile bumpers. However, in the application, corrosion and abrasion resistance are also important. An example of electrodeposition used primarily for corrosion protection is zinc plating on such steel articles as nuts, bolts, and fasteners. Since zinc is more readily attacked by most atmospheric corrosive agents it provides galvanic or sacrificial protection for steel. An electrolytic cell is formed in which zinc, the less noble metal is the anode, and steel, the more noble one, the cathode. The anode corrodes, and the cathode is protected. Deposited metals which are more noble than the substrate, the part up on which the coating is applied, protect against corrosion only if they are completely continuous. Should a small area of the substrate be exposed, it corrodes very rapidly.

An example of an electroplated coating applied primarily for wear resistance is hard chromium on a rotating shaft. To impart desirable electrical properties, gold is often electroplated on contacts, for example. The absence of oxide films, which would raise the electrical resistance, is desired on such contacts. In the case of permalloy, an alloy of iron and nickel plated on copper wires which is used for computer information storage, the magnetic properties are of greater importance.

The electroplating process consists essentially of connecting the parts to be plated to the negative terminal of a direct-current source and another piece of metal to the positive pole, and immersing both in a solution containing ions of the metal to be deposited. The part connected to the negative terminal becomes the cathode, and the other piece the anode. In general, the anode is a piece of the same metal that is to be plated. Metal dissolves at the anode and is plated at the cathode. If the applied current is used only to dissolve and deposit the metal to be plated, the process is 100% efficient. Often, fractions of the applied current are diverted to other reactions such as the evolution of hydrogen at the cathode, which results in lower efficiencies as well as changes in the acidity (pH) of the plating solution. In some processes, such as chromium plating, a piece of metal which is essentially insoluble in the plating solution is the anode. When such insoluble anodes are used, metal ions in the form of soluble compounds must also be added periodically to the plating solution. The anode area is generally about the same as that of the cathode; in some applications it is larger.

Most plating solutions are of the aqueous type. There is a limited use of fused salts or organic liquids as solvents. Non-aqueous solutions are employed for the deposition of metal with lower hydrogen overvoltages; that is, hydrogen rather than the metal is reduced at the cathode in the presence of water.

In addition to metal ions, plating solution contains relatively large quantities of various substances used to increase the electrical conductivity, to buffer, and in some instances, to form complexes with the metal ions. Relatively small amounts of other substances, which are called addition agents, are also present in plating solutions, to level and brighten the deposit, to reduce internal stress, to improve the mechanical properties, and to reduce the size of the metal crystals or grains or to change their orientation.

The quantity of metal deposited, that is, the thickness, depends on the current density (amp/m^2) , the plating time, and the cathode efficiency. The currant is determined by the applied voltage, the electrical conductivity of the plating solution, the distance between anode and cathode, and polarization. Polarization potentials develop because of the various reactions and processes which occur at the anode and cathode, and depend on the rate of these reactions, that is, the current density. If the distance between anode and cathode varies because the part to be plated is irregular in shape, the

thickness of the deposit may vary. A quantity called the throwing power represents the degree to which a uniform deposit thickness is attained on areas of the cathode at varying distances from the anode.

Good throwing power results in the plating efficiency that is low due to polarization where the current density is high. A plating solution such as an alkaline cyanide bath, in which the polarization of the cathode increases strongly with increasing current density, has good throwing power. On the other hand, a plating solution such as an acid sulfate copper bath, which is almost 100% efficient, has poor throwing power.

The other deposition processes are closely related to electroplating; electroless plating and displacement plating. Both processes require no applied current. Electroless plating is a process which once initiated, continues; that is, autocatalytic. Displacement plating occurs when the metal deposited is more noble than the substrate, and the substrate dissolves. The reaction ceases when the substrate is completely covered by a pore-free deposit.

Active Vocabulary

electroplating, dimension, decorative, abrasion, a substrate, to expose, to impart, an oxide film, to divert, to buffer, polarization.

EXERCISES

I. Answer the following questions:

1. What is electroplating? 2. What is electroplating used for? 3. Why can electroplating be applied for corrosion protection? 4. What is an example of an electroplated coating? 5. What does the electroplating process consist of? 6. What can be said about chromium plating? 7. Most plating solutions are of the aqueous type, aren't they? 8. What is called an addition agent? 9. What does the quantity of metal deposited depend on? 10. What other deposition processes are closely related to electroplating?

II. Give Russian equivalents for:

an electroplated coating, to impart properties, undersized parts, a decorative coating, automobile bumpers, abrasion resistance, corrosion protection, steel articles, sacrificial protection, completely continuous, wear resistance, copper wires, a rotating shaft, an oxide film, electrical resistance, essentially insoluble, relatively large quantities, to brighten the deposit, to change one's orientation, an alkaline cyanide bath, good (poor) throwing power, a pore-free deposit.

III. Find in the text word combinations with adjectives in comparative and superlative degrees and translate them.

IV. Read the text with a dictionary and answer the following questions:

1. What are the main steps of electroplating? 2. What is cleaning? 3. What can be said about electrolytic cleaning? 4. What is ultrasonic cleaning? 5. What is cleaning used for?

Cleaning

In order for adherent coatings to be deposited, the surface to be plated must be clean, that is, free from all foreign substances such as oils and greases, as well as oxides or sulfides. The two essential steps are cleaning and pickling.

Three principal methods are employed to remove grease and attached solids. (1) In solvent cleaning, the articles undergo vapor degreasing in which a solvent such as tri- or tetra-chloroethylene is boiled in a closed system, and its vapors are condensed on the metal surfaces. (2) In emulsion cleaning, the metal parts are immersed in a warm mixture of kerosine, a wetting agent, and an alkaline solution. (3) In electrolytic cleaning, the articles are immersed in an alkaline solution, and a direct current is passed between them and the other electrode, which is usually steel. Heavily soiled articles are cleaned in solvent or alkaline spray machines.

Cleaning solutions may contain sodium hydroxide, carbonate, phosphate, and metalsilicate, plus wetting agents and chelating agents. More highly alkaline solutions are used for steel than for other metals. Most of the cleaning is accomplished by the scrubbing action of the evolved gases and the detergency of the components of the solutions. The articles may be connected as anodes, as is usual for steel, or as cathodes, as is usual for other metals. Electrolytic cleaning is usually the last cleaning step.

Ultrasonic cleaning is also used extensively, especially for blind holes or gears packed with soils. Ultrasonic waves introduced into a cleaning solution facilitate and accelerate the detachment of solid particles embedded in crevices and small holes. Frequencies from, about 18,000 to 24,000 H_2 are usually employed. They produce cavitation, which causes rapid local circulation.

V. Read the following text and entitle it:

In this process oxides are removed from the surface of the basis metal. For steel, warm, dilute sulfuric acid is used in large-scale operations because it is inexpensive; but room-temperature, dilute hydrochloric acid is also used for pickling because it is fast-acting. In cathodic pickling of steel, attack of the metal is retarded while the oxide is being dissolved. In addition to rough pickling, acid treatments to activate the surface just prior to plating are often used. Hydrogen embrittlement may be caused by the diffusion of hydrogen in steel during pickling and also in certain plating operations. Especially with high-carbon steels, hydrogen causes cracking (a reduction in the fatigue strength and ductility). Hydrogen is gradually evolved on standing, and more rapidly evolved by heating to about 200°C.

VI. Write the translation of the following text.

Electroforming

Electroforming is a special type of plating in which thick deposits are subsequently removed from the substrate, which acts as a mold. The process is particularly suitable for forming parts which require intricate designs on inside surfaces, for example, waveguides. Intricate machining operations can be performed much more easily on outside surfaces. First, the outside surface of the substrate mold is machined; then, the contours of the design can be transferred to the inside surface of the deposit, and, finally, the deposit is separated from the mold. The mold or matrix can be either metallic or nonmetallic. Nonmetallic molds must be rendered electrically conductive by the application of a powder or by chemical reduction, electroless plating, or vapor deposition. For nonadherent deposits substrate removal is easy; otherwise, the substrate must be dissolved or melted away. Important applications of electroforming are in the production of photograph record masters, printing plates, and some musical instruments and fountain pen caps as well as in waveguides.

VII. Read the text at sight and answer the following questions:

1. What is electrotyping? 2. What does the molding case consist of? 3. What does the electrolytic bath consist of? 4. The cathode electrode is connected with the negative pole of a dynamo, isn't it? 5. Is electrotyping similar to electroplating?

Electrotyping

Electrotyping is the process of producing metal copies of original engraved plates, printing type, woodcuts, half-tones, etc., by means of the electrodeposition of copper upon a mold taken from the original. The molding case consists of a thin plate of lead or copper with a coating of wax about 1/8 in. thick. Mold and original form are warmed and dusted with graphite (black lead) and lampblack so that they may be easily separated from each other. They are then placed in the molding press, which presses the mold and the original together so that the mold bears the pattern of the original. The mold is removed and "built up" by the operator to insure a perfect surface without excess wax. Since wax is a non-conductor of electricity, a film of graphite mixed with water is sprayed over it to make it electrically conductive. It is now ready for the electrolytic bath, which consists of water containing copper sulfate and sulfuric acid, in which are suspended two electrodes. The cathode electrode is connected with the negative pole of a dynamo. The anode or positive electrode consists of bars or plates of copper attached to the positive terminal of the dynamo. The mold is placed in the tank and attached to the cathode. When the current from the dynamo is turned on, the copper anodes are dissolved and move across to the cathode and are there deposited. Since the wax mold is serving as the cathode, it is gradually plated with copper. It requires from two to eight hours for the mold to receive a thin coat of copper. The mold is then removed and the shell of copper is separated by heat from the wax. The back of the copper shell is painted with soldering fluid and coated with solder sheets. It is then backed with molten electrotype metal. After finishing operations to insure perfection of the plate, it is either beveled for use on a patent printing base, or mounted type – high on a word block, if it is to be printed as a mounted plate. "Steel electrotypes" are electrotypes made by substituting nickel bars for the copper anodes in the electrolytic bath, and of course, substituting nickel sulfate for copper sulfate in the solution.

Lead mold electrotypes have sheet lead substituted for wax in the preparation of the mold.

Electrotyping is a chemical process, similar to electroplating. Solutions of acids, bases, and salts in water possess the property of conducting electric current. These compounds are decomposed into their elements. These elements possess electrical charges. The cations, which are the positively charged atoms, proceed to the negative electrode. The anions, or negatively charged atoms, proceed to the positive electrode. Thus, a soluble, possible electrode will gradually be deposited on the negative electrode. The weight of metal deposited on the negative electrode is in proportion to the total quantity of electricity which passes through the solution.

Suggested Topics for Discussion

- 1. Speak on electroplating.
- 2. Speak on cleaning and pickling.
- 3. Speak on electroforming.
- 4. Speak on electrotyping.

CHROMIZING

Chromium and other electrodeposits, enamels, and phosphate coatings on metal surfaces to be protected do not always provide uniform and reliable protection at high temperatures, particularly in cases where differences in thermal expansion may cause spalling. Recourse is then often made to chromizing. In this process a layer of chromium is applied at a temperature causing inward diffusion to form a composition gradient. An important use of chromizing is to protect nickel against a sulfur-containing atmosphere. Chromizing is commonly done by the thermal diffusion of chromium powder, the reduction of chromium oxide or halide in contact, or the thermal decomposition of a chromium halide or carbonyl.

A chromium coating intended for subsequent diffusion treatment can be prepared by immersing an iron base in liquid calcium containing finely dispersed chromium powder. The base loses iron to the liquid while gaining chromium. Another method of creating a diffusion coating of chromium involves decreasing the steel and pickling it in hydrochloric acid, then embedding the steel in chromium powder in a sealed container, and finally heating it to 900–1110°C for up to 2 hr.

Increasing the chromizing temperature within this range sharply reduces the corrosion rate of the product in a moist atmosphere and in kerosine.

Chromium, as well as various other metals, can be codeposited with iron by electroless plating done from an alkaline solution containing a hydrophosphite reducing agent and a KNa tartrate complexing agent.

Active Vocabulary

enamel, expansion, spelling, recourse, to immerse, to pickle, to polish, to embed, to seal, to sputter, uniform, inward.

EXERCISES

I. Answer the following questions:

1. Do chromium and other electrodeposits always provide reliable and uniform protection at high temperatures? 2. What is chromizing used for? 3. What is a chromium coating intended for? 4. When does the base lose iron to the liquid? 5. Under what conditions can chromium be deposited with iron?

II. Give Russian equivalents for:

phosphate coating, to provide uniform and reliable protection, thermal diffusion, a composition gradient, to cause spelling, inward diffusion, a sulfur-containing atmosphere, subsequent diffusion treatment, finely dispersed chromium powder, hydrochloric acid, a sealed container, within this range.

III. Find in the text the names of chemical substances and translate them. IV. Translate the following words of the same root:

1) reduction, to reduce, reductive;

2) diffusion, to diffuse, diffusive;

3) creation, to create, creative.

V. Make up sentences of your own with the following words:

enamel, recourse, to embed, to polish, to pickle, to immerse.

VI. Find in the text attributive groups and translate them.

VII. Find in the text verbals, state their functions and translate the sentences with them.

VIII. Read the text with a dictionary and answer the following questions:

1. Under what conditions is the number of competing oxygen molecules great? 2. Why doesn't the presence of helium interfere with the evaporative deposition of a metallic chromium film? 3. What causes increases in resistivity?

Vacuum Deposition

Chromium to be sublimed for vacuum deposition is commonly first electroplated onto a tungsten filament which can then be electrically heated to the desired temperature of sublimation.

If evaporative deposition of chromium is done in oxygen at a pressure of 10^{-8} torr (vapor pressure of chromium at 1300°C is $1.8 \cdot 10^{-3}$ torr), the number of competing oxygen molecules reaching a surface of chromium condensation is great. Since oxygen chemisorbs on chromium, a substantial fraction of the deposited film will be chromium oxide. An impringement ratio of O₂ : Cr = 10^{-2} is the maximum that can result in the deposition of chromium films that are essentially metallic. Since helium at $3 \cdot 10^{-3}$ torr is not absorbed, its presence at this pressure, in place of oxygen, does not interfere with the evaporative deposition of a metallic chromium film of nearly bulk resistivity. On the other hand, increases in oxygen pressure above 10^{-6} torr cause chromium vacuum deposits to contain increasing amounts of Cr₂O₃.

Since pure vapor-deposited chromium adheres much more strongly to glass than do most conductive metals, the prior deposit of chromium can act as a resistive substrate on which conductive metals can then be deposited.

An SiO₂ source at 1100°C and a chromium source at 1500°C can vapor-deposit a high-resistivity Cr-SiO film on a substrate at 400° C. Chromium-silicon monoxide films feature resistivity and stability without large negative temperature coefficients. Increases in SiO content cause increases in resistivity, but they are negatively affected by increases in temperature. Organometallic compounds for deposition of Cr, Cr-Mo, and Cr-V coatings on carbon steels and on alloy steels include bis-arene complexes of the coating metals. Such compounds decompose on coming into contact with a surface heated to 350–500°C. The surface is then covered with a film of the corresponding metal or alloy. Although the precipitating metal catalyzes further decomposition of the organic radical and, hence, liberates carbon, which passes into the deposit and tends to embrittle it, this affect can be avoided by additions of dibenzene complexes of the same metals to the original compounds.

IX. Read the text at sight, entitle it and express the main idea of the text.

Conversion coatings, formed by the immersion of a substrate metal in an aqueous solution of chromic acid or of chromate or dichromate salts, are of the two types: (1) those that in themselves deposit substantial chromate films on the substrate metal, and (2) those that merely seal or supplement nonmetallic protective coatings, such as oxide or phosphate. For the deposition to occur, activating tons such as nitrate, sulphate, chloride, or fluoride, must be added. Hydrogen generated when any of the activators attack the substrate reduces some of the chromium lone to form a hydrated "chromium chromate" $Cr_2O_3 \cdot CrO_3 \cdot H_2O$, which deposits on the surface of the substrate if the solution is not too acid. Thus magnesium alloys can be chromated in nearly neutral solutions having either more acidity or more alkalinity. Conversion coatings are decorative, protect cadmium or zinc substrates in rural marine atmospheres, and form a base that bonds readily with many paints. The conversion coat must be removed from zinc prior to soldering but, when rosin flux is employed, it need not be removed from cadmium, copper, or silver.

Words and Expressions

supplement – добавление, дополнение; rural – сельский; marine – морской; paint – краска; rosin – канифоль, древесная смола; flux – флюс, плавень.

Suggested Topics for Discussion

- 1. Speak on chromizing.
- 2. Speak on vacuum deposition.
- 3. Speak on aqueous deposition.

ELECTROPOLISHING

A method of polishing metal surfaces by applying an electric current through an electrolytic bath is a process that is the reverse of plating. The metal to be polished is made the anode in an electric circuit. Anodic dissolution of protuberant burrs and sharp edges occurs at a faster rate than over the flat surfaces and crevices, possibly because of locally high current densities. The result produces an exceedingly flat, smooth, brilliant surface.

Electropolishing is used for many purposes. The brilliance of the polished surface makes an attractive finish. Because the polished surface has the same structural properties as the base metal, it serves as an excellent surface for plating. Electropolishing avoids causing differencial surface stresses, one of the requirements for the formation of galvanic cells which cause corrosion. Because no mechanical rubbing is involved, work hardening is avoided. Contaminants, which often are associated with the use of abrasives and polishing compounds, are also avoided. The surface is left clean and may require little or no preparation for subsequent treatment or use. Electropolishing also minimizes loss of high-temperature creeprupture strength.

In electropolishing, the work is submerged in an electrolyte and connected to the positive terminal (anode) of a source of direct-current (dc) power. The negative terminal is connected to an electrode that will resist chemical interaction with the electrolyte. Carbon is often used. The electrolyte is usually a concentrated acid, although alkaline solutions, dilute acids and salts have been successfully employed.

Active Vocabulary

electropolishing, a crevice, exceedingly, smooth, brilliance, to avoid, differencial, to cause corrosion, a contaminant, an abrasive, to minimize, creeprupture, to submerge, to employ.

EXERCISES

I. Answer the following questions:

1. What method is called electropolishing? 2. What is electropolishing used for? 3. Why is work hardening avoided in the process of electropolishing? 4. What chemical substances are used in electropolishing?

II. Give Russian equivalents for:

protuberant burrs, sharp edges, a locally high current density, an exceedingly flat surface, an attractive finish, an excellent surface, to cause surface stresses, mechanical rubbing, polishing compounds, subsequent treatment.

III. Make up sentences with the following adjectives:

protuberant, sharp, flat, high, brilliant, smooth, attractive, excellent.

IV. Find in the text sentences with verbals, state their functions and translate the sentences into Russian.

V. Write the outline of the text and retell it.

PART II

TEXTS FOR ADDITIONAL READING

INVENTORS AND THEIR INVENTIONS

New inventions appear every day to make our lives easier, longer, warmer, and so on. But only a few inventors design a new machine or product that becomes so well known that the invention, named after its creator, becomes a household word. Here are some famous inventors and the inventions that are named after them.

(household – повседневный; creator – создатель).

Rudolf Diesel (1858–1913), a German engineer who invented the diesel engine in 1897 and so began a transport revolution in cars, lorries and trains.

(lorry – грузовик; engine – мотор, двигатель).

Hans Wilhelm Geiger (1832–1915), a German physicist. In 1906–1909 he designed a counter for detecting radioactivity. This was the beginning of modern geigers or geiger counters.

(counter – счетчик; to detect – обнаруживать).

Charles Mackintosh (1766–1843), a Manchester textile chemist who in 1823 developed a rubber solution for covering fabric which led to the production of waterproof raincoats, or mackentoshes.

(rubber solution – резиновый раствор; to develop – создать; waterproof – водонепроницаемый).

Samuel Finley Morse (1791–1872), an American portrait painter who invented the telegraphic short sound /./, long sound /-/-alphabet known as Morse code.

(sound – звук; Morse code – азбука Морзе).

Do you know that until just over a hundred years ago there was no such instrument as the saxophone? It was invented by a Belgian musician Adolphe Sax (1814–1894).

Answer some questions about scientists and inventions of the past:

1. What Russian scientist formulated for the first time the law of conservation of matter and movement? How is this law called now?

2. Do you know the name of the outstanding Russian engineer, designer and inventor who

- made one of the most remarkable watches of all times, an "18-th century miracle";

- built an optic telegraph;

- built the first self-propelled boat;

- made several projects for a single-span (одноарочный) wooden bridge across the Neva, etc?

3. Who was the man who designed the first practical reflecting telescope?

4. Who was the first to establish that Venus was surrounded by an atmosphere of air?

5. How many Faraday's laws of eletrolysis do you know?

6. Who is considered to be the father of electric motor?

7. What country is called the mother of aviation? Whose aeroplane was the first plane in the world?

8. Synthetic rubber was produced in Russia in 1910. Who was the author of this invent on?

9. Do you know that except being the inventor of the universal steamengine James Watt invented a copying machine, a method of bleaching, a machine for drying linen, and an instrument for determining the specific gravities of liquids?

10. It is interesting to know how many laws were introduced by I. Newton in his book "The Principia" (Mathematical Principles of Natural Philosophy)?

A FEW UNITS NAMED AFTER FAMOUS SCIENTISTS

Words like *volt* or *watt* have become part of our language so completely that we sometimes forget that these are the names of famous scientists.

Let us recall a few such units...

An ampere is the unit of electric current in common use. It is that current which, when passed through a solution of silver nitrate in water, will deposit silver at the rate of 0.001118 grams per second. The unit is named after Andre-Marie Ampere (1775–1836) a famous French physicist and mathematician.

A bel is a unit for comparing two values of power. It is ten times the size of the more frequently used decibel, which is used as a measure of response in all types of electrical communication circuits. The unit is named after Alexander Graham Bell (1847–1922), the American inventor of the telephone.

A coulomb is a unit of electric charge equal to the quantity of electricity transferred in one second by a current of one ampere. It is named after Charles Augustin de Coulomb (1736–1806), a prominent French physicist.

A curie (Cu) is the unit of the measurement of radioactivity. It is named after Pierre and Marie Curie, French physicists.

A farad is a unit of electrical capacitance. It is named after Michael Faraday (1791–1867), a famous English physicist.

A gal is a unit of acceleration used in describing the effects of gravity. It is an acceleration of one centimetre per second each second. The unit is named after Galileo Galilei (1564–1642), a famous Italian scientist.

A kelvin is a degree on the thermometric scale that takes absolute zero as its starting point (0 K). It is named after William Thomson (1824–1907), who later became Lord Kelvin, a British professor, the inventor of mirror galvanometer.

A newton is the unit of force in the metre-kilogram-second measurement system. It is named after Sir Isaac Newton (1642–1727), an English scientist, a professor of Cambridge University.

An oersted is a unit of magnetic field intensity. It is named after Hans Christian Oersted (1777–1851), a Danish physicist.

A roentgen is a unit of radiation. It is named after Wilhelm Conrad Roentgen (1845–1923), a famous German physicist.

A volt is the difference of potential between two points if one joule of work is required to transport one coulomb of charge from one point to the other. It is named after Alessandro Volta (1745–1827), an Italian physicist.

A watt [wot] is a unit of power. It is named after James Watt (1736–1819), the English inventor of a steam-engine.

APPENDIX

UNITED STATES PATENT OFFICE METHOD OF ELECTROPLATING STAINLESS STEELS AND IRONS

My invention relates to improvements of electroplating stainless steels and irons. All metals which are electroplated on a ferrous base under any of the present methods of plating offer little protection against the ultimate corrosion of such base due to the fact that the platings are crystalline in structure and vary in porosity, depending either on the metal itself or its method of application.

I form the oxide film on the stainless steels and irons by treating the material in a hot solution of sulfuric acid, water and an etching inhibiting agent, preferably an etching inhibiting oxidizing agent. The quantity of sulfuric acid employed should be such that, when combined with the water and, in the absence of the inhibiting agent, it will quickly attack and rapidly dissolve a-thin specimen of the steel to be filmed when immersed therein. The quantity of the etching inhibiting agent which may then be added to the sulfuric acid water solution should be at least sufficient to prevent the etching of the steel when immersed therein and when said solution is at the temperature to be used in the treatment, which is preferably comparatively high, say from 180 to 220°F. Temperatures lower than 180° may be employed, even room temperatures, but the process proceeds much more rapidly within the preferred temperature range stated above.

As an etching inhibiting agent I prefer to use chromic acid and I prefer to form it in the sulfuric acid water solution by incorporating a chromate or a dichromate forming salt therein such, for example, as sodium, potassium or ammonium dichromate. However, it is to be understood that chromic acid may be added as such to the sulfuric acid water solution. Where chromic acid per se is employed the sulfuric acid water solution is preferably activated by dissolving therein a small portion of scrap metal of the type to be treated before the chromic acid is added, or by adding small quantities of iron and chromium sulfates.

The quantity of free sulfuric acid in the solution as finally formed, if the chromic acid is formed in the solution by adding a chromate or dichromate, is somewhat less than that in the initial sulfuric acid water solution due to the chromic acid forming reaction, and the final bath employed may contain the following ingredients in about percentages stated:

Ingradianta	Percentage
ingreutents	by weight
Water	40 to 50
Free sulfuric acid (1.84 sp. gr.)	30 to 50
Chromic acid	6 to 10
Iron sulfate	0.1 to 1
Chromium sulfate	1 to 2
Other sulfates or bisulfates and impurities	Balance

By simply immersing the article to be plated in one of the above solutions, preferably with the solution at a temperature from 180 to 220°F, for from 20 to 40 minutes, depending somewhat upon the analysis of the alloy, the surface treatment to which it has been subjected, and the temperature of the solution, a film of dark colored oxides is formed substantially integral with the surface of the metal. Such a film contains oxides of the elements in the alloy, such as iron, chromium and nickel but the treatment does not in any way affect the surface texture and finish of the metal. That is to say, if the surface



is highly polished the oxide film will be highly polished; and if the surface is matte, the oxide film will be matte. This film is extremely thin and its thickness is measurable only in Angstrom units. After the film forming treatment the article should be washed to remove the acid and, before plating, especially where the oxidized surface is smooth, as in the case where the surface finish of the base metal before oxidation is very smooth, the article should be given a quick anodic dip in a solution of sodium hydroxide at ordinary room temperature and at a low current density, to insure that the surface of the oxide film is chemically clean. The anodic treatment however must not be such, or so long continued, as to remove the oxide film. A plating of copper, zinc, nickel, chromium, cadmium, gold, silver or any other metal susceptible to electroplating may then be applied thereto by any of the well known, appropriate, electroplating processes for metal to be plated. However, in plating with copper an alkaline electrolyte should be employed because the commonly used copper sulfate-sulfuric acid solution attacks the oxide color film and also the metal beneath the film. Furthermore, the iron in the base material tends to throw the copper out of solution.

The drawing is a fragmentary cross section of a plated sheet which is drawn to a greatly exaggerated vertical scale.

In the drawing represents the ferrous base while 2 and 2' indicate the oxide film on each side thereof, and 3 is the outer layer of plating, here shown on only one side of the base.

While the surfaces of stainless steels are inherently highly resistant to corrosion, they are subject to rusting and pitting when exposed to attack by certain media. However, the corrosion resistance of steels and iron containing chromium in a quantity, say 7 or 8%, by weight, sufficient to withstand treatment in the sulfuric acid water-inhibitor solution in the manner which I have described, is very greatly enhanced by the presence of the dark colored oxide film formed thereon by said treatment, and bleeding or seepage of rust from the iron base through the plating overlying said oxide film is substantially prevented.

What I claim is:

The method of plating the surface of a stainless steel alloy containing at least 7%, by weight, of chromium which comprises forming in and integral with said surface an adherent, dark colored film of oxide by merely immersing said steel in a solution containing, by weight –

Ingredients	Percentage
Water	35 to 55
Free sulfuric acid (1.84 sp. gr.)	15 to 56
Chromic acid	2 to 20
Iron sulfate	0.01 to 10
Chromium sulfate	0.01 to 10
Minor quantities of other sulfates, bisulfates and impuritie	s Balance
and thereafter electroplating said oxide filmed surface w	ith copper in an
alkaline electrolyte.	

THE ELECTROCHEMICAL CELL

(based on Pine Instrument Company papers)

When performing electrochemical experiments in the instructional laboratory, the student and instructor must be aware that these lab EXERCISES require a somewhat greater level of care than the average titrimetric, gravimetric, or spectroscopic assay. The glassware is cleaner, the concentrations are smaller, the electrode is polished, and the solvents are purer. Nevertheless, there is no reason why undergraduate students cannot successfully use a variety of electrochemical techniques in their laboratory work. What follows here is a description of the kinds of apparatus and chemical reagents needed for most voltammetric experiments.

Glassware

In its simplest form, the electrochemical cell is a single piece of glassware capable of holding an appropriate volume of a test solution containing one or more electroactive analytes. Immersed in this solution are three electrodes (working, reference, and auxiliary) that are also electrically connected to a potentiostat. Custom glassware designs that include convenient fittings for mounting electrodes, gas inlets and outlets for purging oxygen, temperature jackets, and/or separate chambers for each of the three electrodes are often used in research environments, but common laboratory glassware can also be adapted for use. When choosing glassware for the instructional laboratory, it is important to consider what volume of test solution is to be used, how easily can students "hook up" the cell, and, in the event of an accident, how expensive is it going to be to replace the cell.

The three neck round bottom flask is a readily available and inexpensive piece of glassware that can be used as an electrochemical cell. These flasks can hold a considerable volume of solution, and the neck openings have large enough diameters that most electrodes will fit through them. Each neck on the flask can be used to mount one of the three electrodes. This configuration is well suited for those experiments where the test solution can be safely exposed to oxygen in the air and where isolation of each electrode in a separate compartment is not required.

It is often necessary to eliminate dissolved oxygen from the test solution whenever moderate to quite negative potentials are being applied to the working electrode. At these potentials dissolved oxygen can be reduced, and the resulting undesired cathodic current may interfere with the measurement of interest. A typical benchtop solution to this problem is to use a cell which is airtight except for one or two gas inlets and a single small outlet. An inert gas such as nitrogen is bubbled through the solution to expel any dissolved oxygen. (Usually one of the inlet tubes, designed especially for this purpose, is a capillary tube terminating near the bottom of the solution.) Then, during the course of an experiment, the air space above the solution is blanketed under a positive pressure of inert gas by passing a steady stream of gas through one inlet and then out of the cell through the small outlet.

A four neck round bottom flask can be configured for oxygen removal as follows. Three of the openings are used to mount the three electrodes in an airtight fashion. (Simply sealing the openings with parafilm will usually suffice.) The fourth opening is then sealed using a rubber septum. A small syringe needle is inserted through the septum near the outer edge of the septum. Then, a much longer needle (capable of being pushed through the septum and down into the test solution) is inserted through the center of the septum. Nitrogen gas is passed into the cell through the long needle while the small needle simply serves as the outlet. The long needle is first pushed down into the solution, and nitrogen gas is allowed to bubble through the solution. Then, when it is time to perform an experiment, the long needle is pulled out of the solution (but not all the way out of the cell), and a blanket of nitrogen gas then covers the solution.

A cell is available from Pine Instrument Company that is well suited for use in an instructional laboratory. The cell has a volume of 125 mL and has five openings. Three of these openings have ground glass joints and can be used to mount the working, reference, and auxiliary electrodes. Sleeve mounts made just for this cell are also available that allow popular reference electrodes to be mounted to the cell. The other two openings are screwthread type and accept 6 mm diameter glass rods mounted using an o-ring seal. These are intended for glass tubing that connects the cell to the inert gas supply. These openings can also be used to mount electrodes fashioned from 6 mm glass tubing.

The Test Solution

The test solution inside the electrochemical cell consists of one or more analytes dissolved in a conductive electrolyte solution. The electrolyte solution usually consists of a (relatively) large concentration of an electrochemically inert salt dissolved in an ultra-pure solvent. The purity of the solvent is very important because the sensitivity of most voltammetric techniques is such that even a trace amount of an electroactive contaminant will show up. Even a cursory reading of the electrochemical literature reveals the great lengths taken by research electrochemists to insure the purity of their chemical systems. It is not uncommon to find them using nonaqueous systems based on HPLC grade organic solvents that have been rigorously dried and in some cases triply distilled.

The instructor of an academic instructional laboratory, however, is probably more interested in saving as much time and money as possible by using a solvent that is inexpensive and readily available. The obvious choice is to use water, and the experiments in this manual are designed to use aqueous electrolyte solutions. Reagent grade acids and bases, diluted to appropriate concentration levels, make excellent solvents for electrochemistry. Similarly, various buffers and inert salt solutions may also be used. In all cases, however, the solution must be prepared from very pure water and the glassware used must be very clean.

These aqueous electrolyte solutions are in many cases available at the required purity and electrolyte levels directly from major chemical manufacturers. Some instructors (running large laboratory programs) may find that it is easiest simply to order a bulk quantity of the required electrolyte solution and distribute it to the students as needed. In many cases, however, the aqueous electrolyte solutions will have to be prepared "in-house", either by a lab technician or by the students themselves. In these cases, it is very important to have a source of ultra-pure water for making and diluting solutions.

Most undergraduate analytical laboratory programs make extensive use of some kind of purified water source. While this "pure" water from singlestage distillation of the local municipal water supply is quite adequate for spectroscopic and titrimetric experiments, it is generally ill-suited for voltammetry. Water of the highest purity can be obtained from more expensive water filtration systems that make use of ion-exchange columns, and instructors with access to such systems may find this water source most convenient, in smaller academic settings, however, it is probably most cost-effective to simply purchase deionized, ultrafiltered (DIUF) water or HPLC grade water from a major chemical manufacturer. Most manufacturers offer this ultra-pure water in various quantities including 20 liter carboys which are well suited for undergraduate use.

The *supporting electrolyte* present in the electrochemical test solution is put there to increase the conductivity of the solution. This helps diminish the magnitude of the electric field across the (bulk) test solution which, in turn, helps eliminate (undesired) movement of the analyte under the impetus of this field. The potential drop between electrodes in the cell remains the same as it would be for a non-conductive solution, but the added electrolyte causes most of the potential drop to occur within a few nanometers of the electrode surfaces.

The electric field across the bulk of the solution is never entirely eliminated, of course, but it is generally accepted that if the concentration of the supporting electrolyte is at least one hundred (100) times greater than that of the analyte, then the effect of the electric field on the analyte's motion can be safely neglected. In practice, the supporting electrolyte concentration is anywhere between 0.1 M and 1.0 M, which means that analyte concentrations rarely exceed 0.01 M in voltammetry experiments.

The choice of supporting electrolyte is generally based on two questions: (1) is it soluble in the solvent being used? and (2), is it electrochemically inert over the range of potentials being used? When using water as a solvent, one of the best choices for supporting electrolyte is potassium nitrate (KNO₃), which is quite soluble and electrochemically inert. Potassium chloride (KCl) may be used, but chloride ion is susceptible to oxidation at more positive potentials. Solutions of strong acids or strong bases in near molar concentrations also make good solvents for electrochemistry due to their high conductivity. The usefulness of acidic solutions is generally limited by the reduction of hydronium ion at negative potentials.

Preparing Dilute Solutions

The laboratory instructor is presented with a bit of a quandary when contemplating how best to supply students with the necessary reagents and pure solvents for an electrochemical experiment. Given the expense and trouble associated with obtaining a pure enough solvent and the cost of hazardous waste disposal, it seems logical to have the students use a minimum volume of solvent when preparing solutions. But because the analyte concentrations in voltammetry experiments are quite dilute (less than 0.01 M), the student who only has access to a milligram resolution balance is forced to use either a large volume of solvent or multiple dilution steps.

An example is offered which illustrates this point. If an experiment calls for the student to quantitatively prepare 100 mL of a 5.0 mM solution of an analyte with a formula mass of 300.0 g/mole, then the student and/or instructor may choose one of the following three preparation strategies, each of which has advantages and disadvantages associated with it:

a) Accurately weigh 0.1500 grams of the analyte into a 100 mL volumetric flask and then dilute "to the line" using the pure electrolyte solution. A group of ten students, each working alone, would consume only one liter of electrolyte solution using this option.

b) Accurately weigh 1.500 grams of the analyte into a 1000 mL volumetric flask and then dilute "to the line" using the pure electrolyte solution. A group of ten students, each working alone, would consume ten liters of electrolyte solution using this option.

c) The instructor prepares a "stock" solution by accurately weighing 7.500 grams of the analyte into a 500 mL flask and diluting "to the line" with the pure electrolyte solution. Then each student pipettes 10.00 mL of the stock solution into a 100 mL volumetric flask and dilutes "to the line" using the pure electrolyte solution. A group of ten students, each working alone, would consume only 1.5 liters of electrolyte solution using this option.

The first strategy has the two-fold advantage of using the minimum volume of expensive electrolyte solution while enjoying the precision associated with just one dilution step. However, in order to prepare the solution with at the required precision, a balance capable of reproducibly measuring to the nearest microgram must be available. The cost of digital microbalances has been dropping in recent years, so that this option may soon be widely available. The second strategy retains the precision associated with just one dilution step but does not require a microbalance. Unfortunately, if each student prepares a separate solution, this option wastes nine liters of electrolyte solution! Of course, if the entire group of ten students use the same one liter batch of solution, there would be no waste, but there would also be no accountability on the part of each student for the accuracy of the experimental results.

The last strategy is probably the best option when no microbalance is available but the instructor desires to maintain some level of student accountability. It uses an acceptably low volume of electrolyte solution and still requires each student to prepare separate solutions. The primary disadvantage is that the instructor must prepare the stock solution ahead of time.

Choice of Working Electrode

The ideal working electrode is a very clean metal surface with a well-defined geometry that is in direct contact with an electrochemical test solution. Working electrodes intended for general purpose work are usually made from a metal that is electrochemically inert over a wide range of potentials. The most widely used metals are mercury, platinum, gold, and various forms of carbon. Solid metals are typically fashioned into disks surrounded by a chemically inert shroud made from Teflon, glass, or epoxy. Mercury, being a liquid, tends to be used as a spherical droplet in contact with the solution. There are pros and cons associated with each type of working electrode material, and each is discussed in some detail below.

The size and shape of the electrode surface also has an effect on the voltametric response of the electrode. The overall current observed at an electrode is directly related to its surface area, and disk shaped electrodes with diameters greater than 100 μ m, or *macroelectrodes*, generally produce easily measured currents in the microamp to milliamp range. Electrodes with dimensions less than 100 μ m are generally referred to as *microelectrode*, and these typically produce currents in the picoamp to nanoamp range. Although the overall currents observed at microelectrodes are small enough to require specialized electrochemical equipment, these electrodes enjoy a greater signal-to-background ratio and, being small, find uses in applications where the sample size is quite small.

Mercury Electrodes

The classic polarography described in most undergraduate textbooks makes use of a liquid mercury as a working electrode. In its most common incarnation, the *dropping mercury electrode*, a reservoir of mercury is allowed to slowly drain through a vertical capillary tube immersed in the electrochemical test solution. As the mercury slowly exits from the capillary, it forms a small drop with a nearly spherical shape that is in contact with the test solution. Electroactive analytes in the test solution undergo oxidation or reduction reactions at the surface of the drop.

This electrode configuration enjoys quite a few advantages including a very long history of use and an electrode surface that is easily reproducible. Indeed, in the event that the surface of the mercury drop becomes fouled, the drop is simply allowed to fall into the test solution, and a fresh drop is allowed to form at the capillary tube's exit. In aqueous solutions, the mercury electrode can be used at more negative potentials than other metals without interference from the reduction of hydronium ion. Finally, the mercury electrode plays an important role in *stripping voltammetry-a* technique which relies on preconcentrating one or more analytes into a mercury electrode and then separately electrolyzing (or stripping) each individual analyte out of the electrode.

The single biggest disadvantage of the dropping mercury electrode in the undergraduate laboratory is its toxicity. Students must be cautioned ahead of time about the hazards associated with mercury, and provision must be made for proper collection and disposal of the mercury used during an experiment. In addition, undergraduates who find the mercury drop electrode apparatus difficult to operate may lose track of the point of an experiment.

An alternative to the mercury drop electrode is a *mercury film electrode* (MFE). A glassy carbon disk electrode is placed in an electrochemical test solution that contains some mercury (H) nitrate, then by holding the electrode at a sufficiently negative potential, a thin film of mercury will coat its surface. An MFE formed in this fashion is suitable for use in a stripping voltametry experiment, and the small quantity of mercury involved poses less of a hazard in the undergraduate laboratory

Platinum Electrodes

Despite the expense associated with this precious metal, platinum is one of the most widely used materials for fabricating working electrodes. Platinum has the advantage of being an easily machined metal that is electrochemically inert. In aqueous solvent systems, the platinum working electrode is a good choice when working with positive potentials, but at negative potentials, interference from the reduction of hydronium ion is a problem. In rigorously anhydrous organic solvent systems, platinum is the best and most popular choice for the working electrode material due to its wide potential window in both the positive and negative directions. Large diameter platinum macroelectrodes are generally fabricated by welding a thick platinum disk to the end of a brass rod, machining the platinum disk and brass rod so that they are concentric, and then placing a Teflon shroud around the entire assembly. The platinum surface is then ground to a mirror quality finish using a polishing paste that contains sub-micron alumina particles. As with all solid metal electrodes, the surface must occasionally be repolished to remove surface contaminants picked up during experiments.

Smaller diameter platinum disk electrodes and platinum microelectrodes are usually fabricated by shrouding a short length of platinum wire in soft glass. The diameter of the resulting platinum disk is the same as the diameter of the wire used. Because of the hardness of the glass shroud, these electrodes are usually polished to a mirror finish using polishing paste that contains sub-micron *diamond* particles.

The platinum working electrode is an excellent choice for the undergraduate laboratory. Of the solid metal electrodes, it is definitely the most popular due to its applicability to a wide range of electrochemical systems. It is durable and long lasting, and even an undergraduate can be taught how to properly polish it when required. Its primary disadvantage is that it has a limited use at negative potentials in aqueous solutions.

Gold Electrodes

Gold working electrodes are designed along the same lines as platinum working electrodes Gold is usually less expensive than platinum, but it is not as electrochemically inert. The surface of a gold electrode is subject to oxidation at moderately positive potentials, and so it is not as generally useful as platinum.

Carbon Electrodes

Various forms of carbon are used as working electrode materials. Carbon electrodes are useful over a fairly wide potential window in both the positive and negative directions, and their principle advantage over platinum electrodes is the ability to work at more negative potentials in aqueous solutions. Solid carbon electrodes are usually made from *glassy carbon* or *pyrolytic graphite*, both of which are fairly expensive materials that are more difficult to machine than platinum or gold. The surface of a carbon electrode usually needs to be polished quite frequently, and the surface sometimes has to be "activated" by various empirical methods in order to obtain maximal performance from the electrode.

A less expensive carbon electrode can be fashioned using *carbon paste*. A cylindrical recess is drilled into a Teflon shroud, and an electrical contact is placed in the back of the recess. Each time the electrode is to be used, the recess is packed with a paste that contains carbon particles, and then the paste is carefully polished to a smooth disk-shaped surface. Working with a carbon paste electrode is technically more demanding because the paste can be gouged inadvertently after being polished.

Rotated Electrodes

A special class of electrochemical techniques, known as *hydrodynamic* methods, actually involve the use of spinning working electrodes. Typically, a specially designed glassy carbon or platinum disk electrode is attached to the end of a rigid shaft, and then this shaft is mounted on a high speed motor. These electrodes are immersed in a test solution and rotated at several thousand rotations per minute. A characteristic "vortex-like" solution flow pattern emerges as a result of the electrode's motion.

Because the solution is constantly stirred, fresh analyte solution is always being conveyed to the region near the surface of the electrode. This steady flow of analyte allows what is known as a "steady-state current" to flow at the rotating electrode as analytes are either oxidized or reduced. Steady-state currents are generally quite easy to measure because they remain constant with respect to time. (In most other electrochemical methods, currents tend to decay with time as the supply of analyte near the electrode is depleted.)

When using a rotating electrode, it is important that the cell volume be large enough to sustain a rapidly spinning solution flow. Also, the opening at the top of the cell must be large enough for the shaft of the rotating electrode. This means that the cell contents are open to the air, making oxygen removal difficult. A strong flow of inert gas is required to blanket the solution whenever a rotating electrode is being used to study an air-sensitive electrochemical system.

Electrical contact to a rotating electrode is usually made with brushes that are in mechanical contact with the rotating shaft. If the brushes or the shaft are dirty, experimental results will be obscured by a rapid, but periodic noise source. If this happens, the brushes should be cleaned or replaced, as needed.

Choice of Reference Electrode

The potential of a working electrode in a voltammetry experiment is always controlled with respect to some standard, and that standard is the reference electrode. While the thermodynamic scale of half-reaction potentials found in most textbooks measures electrode potentials against the "standard hydrogen" reference electrode (SHE), in actual practice the SHE is much too cumbersome to use. For this reason, a number of other reference electrodes have been developed. Experimental measurements of potential are made against these alternate reference electrodes, and then the potentials are "corrected" by simple addition or subtraction and reported against the SHE.

One of the most generally available reference electrodes for work in aqueous solutions is the *saturated calomel electrode* (SCE). The half reaction that occurs inside of an SCE reference is given below.

$$Hg_2Cl_2(s) + 2e^- \leftrightarrow 2Hg(/) + 2Cl^-(aq).$$

At 25°C, the formal potential for the SCE half reaction lies 0.2415 volts more positive than the SHE reference electrode. A potential measured against using an SCE can be reported versus the SHE simply by adding 0.2415 volts to it.

The SCE electrode must be constructed in an appropriate piece of glassware that can keep a small amount of mercury in direct contact with solid calomel (Hg₂Cl₂) paste while at the same time keeping the paste in contact with a saturated aqueous solution of potassium chloride. The short hand notation for the SCE half cell is as follows:

Electrical contact is made by immersing a platinum wire into the liquid mercury, and the potassium chloride solution maintains ionic contact with the test solution in the electrochemical cell via a salt bridge or porous glass frit. Such electrodes can be "home made" or purchased from a variety of manufacturers.

Other useful reference electrodes are based on half reactions involving a silver electrode. For work in aqueous systems, the "silver-silver chloride" or Ag/AgCl reference is quite popular. The half reaction for this reference electrode is as follows:

$$\operatorname{AgCl}(s) + e \leftrightarrow \operatorname{Ag}(s) + \operatorname{Cl'}(aq).$$

The actual potential assumed by an Ag/AgCl reference depends only on the activity of the chloride anion. (The other two species appearing in the half-reaction are solids which always have unit activity.) To serve as a reference, the chloride activity needs to be held constant. To accomplish this, a silver wire (coated with a layer of silver chloride) is immersed in an internal solution saturated with potassium chloride. The chloride ion concentration remains fixed at the saturation limit. The short hand notation for this reference electrode half cell is given below:

Electrical contact is made by direct connection to the silver wire, and the internal electrode solution is placed in ionic contact with the test solution via a salt bridge or porous glass frit.

The Auxiliary Electrode

In traditional two electrode cells that have only a working electrode and a reference electrode, current is necessarily forced to flow through the reference electrode whenever a measurement is made. If enough current flows through a reference electrode, its internal chemical composition may be significantly altered, causing its potential to drift away from the expected standard value. For this and other reasons, it is desirable to make electrochemical measurements without current flowing through the reference electrode. Modern three and four electrode potentiostats use a feedback circuit to prevent this from happening, but this feedback circuit requires that an additional *auxiliary* electrode be introduced into the electrochemical cell. This auxiliary (or counter) electrode provides an alternate route for the current to follow, so that only a very small current flows through the reference electrode.

The auxiliary electrode can be made from just about any material using any desired electrode geometry. Design choices are usually based on finding a material that is chemically inert in the particular test solution being studied, and it is generally a good idea for the auxiliary electrode to have a large surface area. In most cases, a coil of platinum wire is used, but stainless steel, copper or aluminum wire may work in non-corrosive solutions where metal cation interference is not a concern. If the electrochemical cell is made of metal, then the cell itself might be used as the auxiliary.

Because current flows at the auxiliary electrode, electrochemical processes will also occur there. If the working electrode is reducing something, then the auxiliary electrode must oxidize something, and vice versa. The products generated at the auxiliary electrode, if allowed to diffuse to the working electrode, may interfere with the experimental measurement. When this is a problem, the auxiliary electrode is placed in a separate compartment containing an electrolyte solution that is in ionic contact with the main test solution via a glass frit. In most cases, however, the auxiliary can be placed right in the test solution along with the reference and working electrodes.

Electrical Shielding

The small currents observed in some electrochemical experiments are subject to interference from electrical noise in the laboratory environment. To help shield the experiment from noise, it is a good idea to use coaxial cable to make all connections from the electrodes to the potentiostat, and if using a plotter, the connections between it and the potentiostat should use coaxial cable as well. These simple measures usually reduce noise to an insignificant level.

When using very small electrodes or low analyte concentrations, it is likely that the current observed at the working electrode will on the order of nanoamps to picoamps. When measuring such small currents, it is usually necessary to place the entire cell inside of a metal cage to shield the cell from the noisy laboratory environment. Sometimes called a "Faraday cage", the metal cage should be grounded to the same point that the potentiostat and output device are grounded.

An undue amount of noise can often be traced to the reference electrode. Because the reference electrode is necessarily a high in impedance, it can serve as an antenna for picking up electronic noise. Also, bubbles or clogged frits within the reference electrode are particularly common sources of noise.

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