STUDY OF ELECTRICAL BEHAVIOUR AND SPECTRAL EMISSIONOF MOLECULES IN THE INTERFACE OF SOLID AND LIQUID

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Abstract:
Measurement of the intensity of radiation emitted by dc glow discharge as a function of discharge current carried out for the different electrolytes along with V-I characteristics. The voltage-ampere characteristics during a glow discharge in the atmospheric pressure gas using an electrolytic solution as the anode and metal electrode like tungsten as a cathode were carried out. Under the study of glow discharges of various elements, a monochromatic light at various wavelengths generated. Few species shows a change in the color of the glow when discharge current increased. Investigated the negative resistance of different electrolytic solutions. This behavior investigated as tunneling behavior of electrolytic solution using DC glow discharge. The dc glow discharge spectrometry is the most essential part of the electrical and spectral emission studies of the molecules, atoms and ions in the interface of solid and liquid.

Keywords: *monochromatic, tungsten, negative resistance, emission, metal, discharge*

Introduction:

Phenomenon of discharge of electricity through the study of property of ionized gases has proved to be fruitful for the investigation. DC glow discharge with liquid electrodes have wide practical applications due to its simple technique.Electrical and spectral characterization of the glow discharge[1-7] of the material helps in studying the chemical composition of the material. The elements in the material may be excited in the plasma [8, 9.12] produced between liquid and solid interface. The neutral atoms, ionized atoms and molecules are excited and they emit characteristic spectrum and hence atomic, ionic or molecular species may be identified. Spectral study of the glow discharge [3, 4, 7, and 10] of the material helps in studying the chemical composition of the material. The solid liquid junction is formed when current is passed through the junction; a plasma film is generated along the interfaces between solid and liquid. The plasma pressure is very near to the atmospheric pressure [11, 13, and 14]. The plasma parameters in DC glow discharge may be generated by a current source [15].] The method is very low cost and quick results may be obtained and therefore has wide applications.

When electric discharge is passed to a conducting solution from an electrode, which is placed in the gas space above the liquid surface, reactions take place in the liquid phase and the process is referred to as “Glow Discharge Electrolysis (GDE)”. Traditionally [16] dc-glow discharge optical emission spectroscopy is mainly applied in the materials sciences where it is used for bulk and surface analysis, pellets containing the adsorbed liquid and direct analysis of the liquid samples by use of adequate sample introduction techniques. The dc glow discharge continues to be the subject of spectroscopic research [17] and analytical method development. Glow discharges [16,

18] are used for a variety of technological, physical and analytical applications, ranging from plasma etching and deposition systems in the micro-electronics industry, to lasers or even plasma monitors. Liquids can be analyzed directly at atmospheric pressures, when applying the atmospheric electrolyte cathode glow discharge cell approach with detection by emission spectroscopy as described by Cserfalvi and Mezei [3].
With this background of dc glow discharge system, in this paper a little attempt has been made to study the electrical and spectral characterization of dc glow discharge of the material at the interface of solid and liquid which helps in studying the chemical composition of the material.

Material and Methods:

The experimental arrangement used for the investigation of dc glow discharge is simple and. It is inexpensive arrangement and it is very much cost effective as shown in figure 1. It consists of tungsten electrode of length 40 mm and diameter 3mm fused in glass capillary tube and suspended axially in a hollow slotted stainless steel cylinder, of length 6 cm and internal diameter 2.54 cm. The stainless steel cylinder served as another electrode i.e. anode in the glow discharge. The tungsten electrode can be used as cathode by connecting it to the dc power supply of 700 V capacity having 1.5 A current capacity. In this arrangement the hallow cylinder was dipped in a electrolytic aqueous solution taken in a glass beaker. The depth of immersion of the tungsten electrode in electrolyte solution could be adjusted with the help of micrometer adjustable stand. In this way the solution itself acts as another electrode.

Result and Discussions:

Variation of electrolytic current with the applied dc-voltage during glow discharge in atmospheric pressure gas using 28 electrolytic solutions as the anode and cathode were carried out. The colors emitted on the glow are observed and listed in table 1. As an example we consider the electrolytic aqueous solution of 0.5N Cd $(NO_3)_2.4H_2O$ as the anode, the electrolytic process leading to a luminescent glow is best depicted by the standard voltage-current curve as shown in figure 2.

In the region AB the curve is almost linear, the Ohms law is satisfied and conventional electrolysis found with tiny bubbles of gas around both material electrodes-tungsten electrode and stainless steel electrode. At the voltage corresponding to point B in curve, a smooth evolution of gas bubbles is disturbed and layer of steam is seen at the tungsten cathode. In the region between B and C, the pointer of voltmeter and ammeter widely fluctuates. In this region the characteristics like current passing through the electrode and voltage applied found as unstable.
The behavior of region BC, CD and DE can be explained as follows. Because of increase in the applied dc voltage, the rate of gas evolution is increased with the formation of large size gas bubbles at a fast rate. This decreases the rate of migration of the ions and charge transfer process at the electrodes. When voltage is further increased more fluctuations are obtained in both voltage and current readings with fall in current. This unstable decreased current is shown by line BC. In the neighborhood of point C it is found that fluctuation rate decreases and now hissing sound occurs. When the applied dc voltage reaches to the point C, there is intermittent sparking. The formation of gas bubbles around the tungsten electrode has now stopped. After increasing the applied dc-voltage to a still higher value the formation of movable thin vapor film around the tungsten cathode takes place, which at times produces the vortex motion and visible glow spark of greenish-blue color is found in the gap between cathode and solution phase. Due to vortex motion, electrolyte periodically touches to the tungsten cathode surface. This produces local heating at the tungsten cathode

surface and visible glow spark of bluish-green color. Due to the local heating process there produces the vapor jet and nearby liquid molecules tried to take its place. The region CD of V- I characteristics shows this situation. Thus the region B to C represents the negative slope as seen in the curve. When the electrolyte current decreases to the corresponding point D, the violent gas evolution stops and slope of the curve changes sign from negative to positive. After the point D, with the applied dc voltages the current starts increasing and thereby producing a stable superheated insulating layer around the cathode (tungsten electrode). At this situation a continuous bluish-green glow is developed at the cathode surface. For a further increase in applied dc voltage, the intensity of the glow increases continuously with the increase in current also as shown in figure 2. Thus the region beyond D i.e. along DE appears to be true glow discharge. This happens due to the discharge of accumulated ions through the insulating layer. This situation produces intense glow of bluish-green color and it sometimes can be pictured as corona discharge. Thus under the observation, it is quite obvious that the superheated insulating layer around the cathode is the governing factor responsible for the bluish-green glow.

Tunnel Behavior Under V-I Characteristics of DC-glow Discharge

The discharge parameter like V-I characteristics of dc-glow discharge between the solid and liquid interfaces behaves like that of Tunnel diode. This has been investigated under the observation of V-I characteristics of aqueous solution of different concentrations. The energy band diagrams of cathode type and anode type (plasma band) materials as shown in figure 3. When the cathode type material (tungsten electrode) is joined, the energy band diagram under no bias condition becomes. The junction barrier produces only a rough alignment of the two materials and their respective valence and conduction bands, hence no tunneling occurs. Due to the downward movement of the cathode region, the anode region valence band becomes exactly aligned with the cathode region conduction band. At this stage, electrons tunneling takes place as shown in figure. However when applied voltage increased further, two bands get out of alignment. Thus tunneling of electrons stops thereby decreasing the current.

For this investigation taking the example of V-I characteristics for aqueous solution of 0.5 N KOH by dc glow discharge as shown in figure 4. With initially gradually increasing dc-voltage, the significant electrolyte current rises to its peak value say Ip and the corresponding applied voltage reaches to a value say Vp (at point B).

When applied voltage is increased to a value greater than Vp, the electrolyte discharge current starts decreasing till it achieves its minimum value called valley current Iv corresponding to valley voltage Vv (at point D). For the voltages greater than Vv current starts increasing again as in any ordinary junction diode.

In a similar way to negative resistance of the Tunnel diode it is seen from the figure in the region between peak point B and valley point D that the electrolyte current decreases with increase in the applied voltage. This behavior of the characteristics is similar to the electrolytic cell possesses negative resistance in this region. In fact this contributes the most useful property of the diode. Instead of absorbing power a negative resistance produces power.

Ip/Iv ratio is almost as important factor at the point of view of the negative resistance of electrolyte. It determines the depth of the negative resistance. By adopting the same procedure we investigate the V-I characteristic of twenty seven solutions. Further we obtain the characteristics like Ip, Iv and Ip/Iv ratio with

negative resistance dV/ dI for all the solutions and the results are tabulated in table 2.

Another point worth noting is that this resistance increases as we gofrom point B to D because as applied voltage is increased current keeps decreasing which means that negative resistance of electrolytic cell keeps increasing.

Thus the resistance offered by the electrolyte within the negative-resistance section of its characteristic (shown in figure as shaded) during glow discharge is the reciprocal of the slope of V-I characteristic in this region. The value of the negative resistance Rn = -dV/dI in the region BD depends on the composition of electrolyte (aqueous solution), current and voltage.

Conclusion:

DC Glow discharge using electrolytic solution as the anode and the metallic electrode as the cathode for the study of glow discharge in the atmospheric pressure gas which leads to the investigation of phenomenon of spectrometry shows that, a sensitive and inexpensive technique for the elemental analysis of electrolytic solutions.

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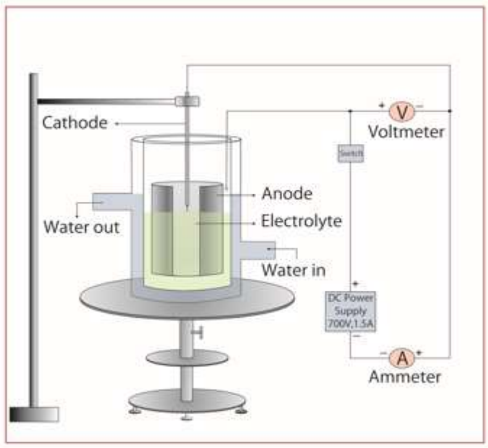

Fig. 1: Experimental arrangement

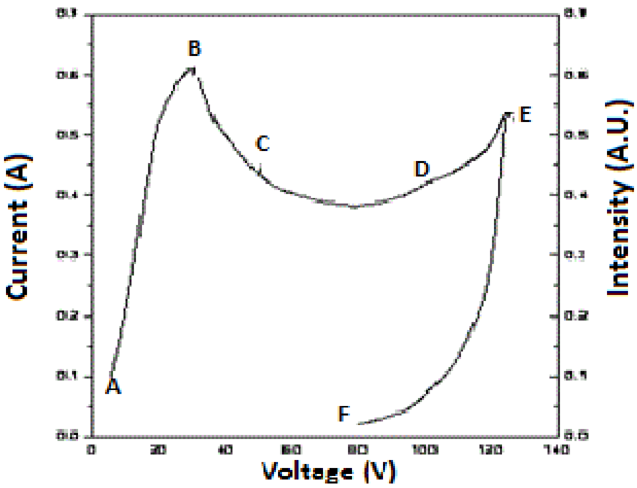

Fig.2: V-I Characteristics of 0.5 N Solution of Cd (NO3)2.4H2O

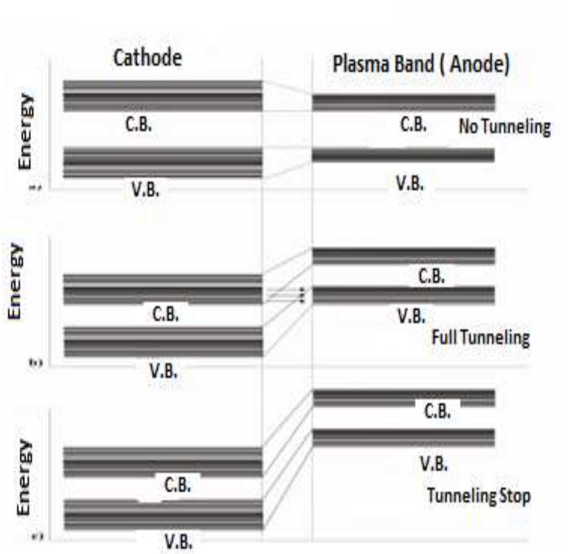

Fig. 3: Energy band diagram

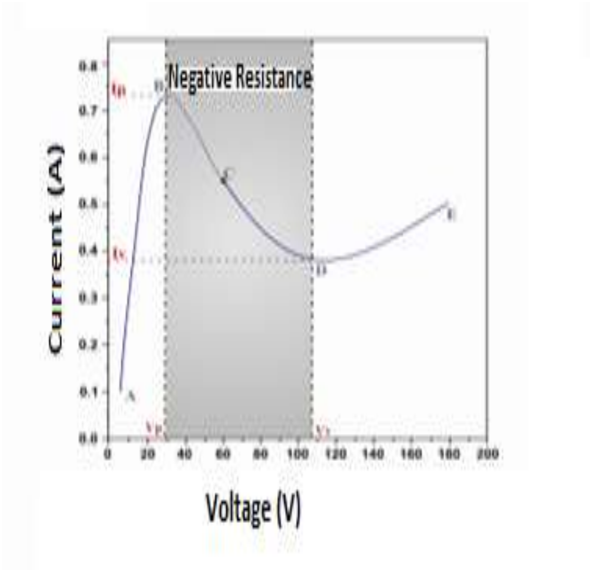

Fig.4: Tunnel Behavior under V-I, Characteristics of KOH solution

Table 1: Color of Discharge Glow

Sr. No	Electrolytic Solution	Color of glow when solution used as	
		Anode	Cathode
1	0.5N NaOH	Yellow	Yellow
2	0.5N KOH	Lavender	Lavender
3	0.25 N LiNO3	Reddish	Reddish
4	0.1N Pb(NO3)2	Bluish	Bluish
5	0.5N MgSO4	Green	Orange
6	0.5N CuCl2.2H2O	Green	White
7	0.05N AgNO3	Pale Green	Yellow
8	0.5N NaCl	Yellow	Yellow
9	0.5N KNO3	Lavendor	Lavender
10	0.5N CaCl2	Orange	Pink

Table 2: Tunnel behavior of electrolytic solution by dc glow discharge

Sr.No.	Electrolytic solution	Ip/Iv ratio	Negative resistance
			Rn = - dV/ dI
1	0.5N FeSO4	1.937	-191.91
2	0.5 N CdSO4	1.645	-141.35
3	0.5 N KCl	1.4366	-175.01
4	0.5 N NiSO4	1.1872	-862.42
5	0.25 N COCl2	1.471	-111.55
6	0.25 N TiO2	1.4759	-316.96
7	0.5N AlCl3	1.5	-250
8	0.5N (NH4)2SO4	1.43	-159.17
9	0.5N KOH	1.9375	-230.88
10	0.5N KNO3	1.7179	-211.74