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Cyclic Voltammetry of Zirconyl Chloride ($ZrOCl_2$) in KF Medium Using Silver Working Electrode (SWE)

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ABSTRACT

The cyclic Voltammetry of zirconyl chloride with different concentrations was measured experimentally using DY2000 cyclic Voltammetry apparatus in 0.1M KF (potassium fluoride) as a supporting electrolyte.

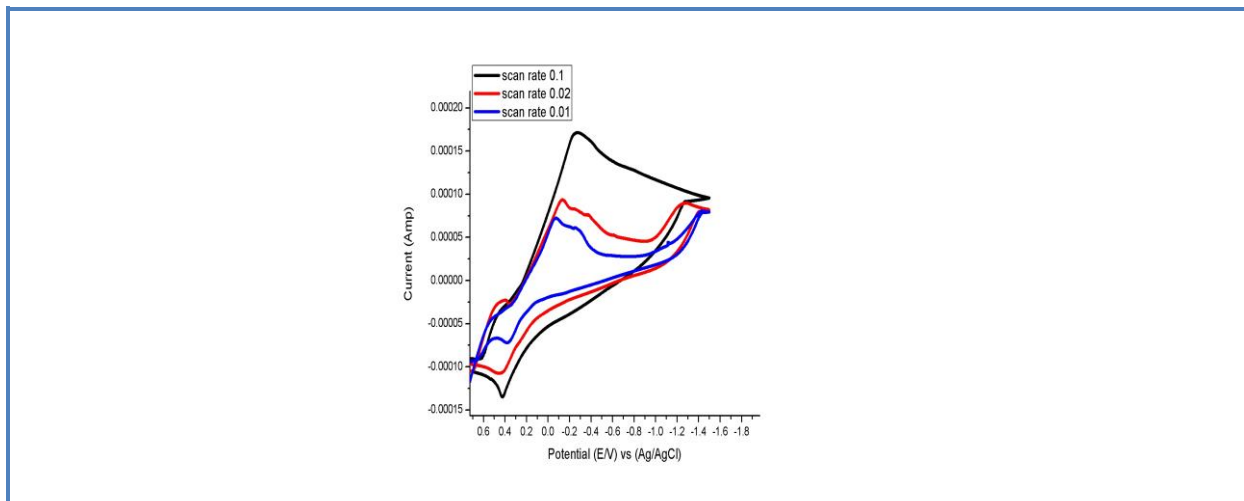
The silver electrode was used as a supporting working electrode. The other two electrodes in the three-electrode system are platinum wire and Ag / AgCl electrode immersed in saturated KCl solution. The redox mechanism was supported by reduction and/or oxidation.

Effect of scan rate was also examined and the redox system is diffusion controlled. The different used scans are 0.1, 0.02 and 0.01 Volt per Sec. The relation between i_p and log scan rate was done to ensure the redox mechanism. It was concluded that zirconyl ions are hydrolyzed in 0.1M KF solutions forming hydroxyl complexes.

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Graphical Abstract



Introduction

Solvent effect and complex stability reaction between metal ions and ligands (organic compounds) can be well explained by the use of cyclic Voltammetry [1]. Metal ion like Zr^{4+} gave reduction wave very far ~ -1.5 [2].

But, using silver metal electrode as the working electrode definite wave at ~ -0.3 was observed.

Here, we prepared, in our laboratory, silver electrode with diameter 0.2 mm jointed to copper wire and then covered by heat shrink polymer. This silver electrode is a very good electrical conductor and therefore was used as SWE (working electrode).

Materials and Methods

The chemicals used $ZrOCl_2$, KCl is from Sigma Aldrich Co. and used directly without purification.

DY2000 cyclic Voltammetry apparatus was used for measuring the voltammograms at different scan rates. Highly purified water is used in practical preparation and measuring of the solutions. Devotion with nitrogen for 10 minutes was applied to the measured solutions.

Three electrodes system was used for processing the cyclic voltammograms. Moreover, Ag / AgCl in saturated KCl was used as a reference electrode and platinum wire as auxiliary electrode to protect the working procedure for the working electrode.

Results and Discussion

Redox behaviour of $ZrOCl_2$ in KF solutions:

The electrochemical behavior and redox processes of Zirconyl chloride in 0.1 M KF were studied at the silver electrode in the range from 0.5 till -1.5 V.

The cyclic waves examined by equation (1) :

$$i_p = (2.69 \times 10^5) n^{3/2} AD^{1/2} v^{1/2} C \quad (1)$$

Where i_p is the current in Ampere, A is a surface area of the silver electrode in cm^2 , D is the diffusion coefficient in cm^2/sec , v is the rate used volts/second and c is the molar concentration.

The current measure depends on the movement of electroactive material to the surface of the working electrode and the electron transfer reaction.

The stationary electrode used the diffusion, was the principal transfer of reactants to working electrode, and was also accompanied by slow mass transfer. As a result, the rate of mass transfer decreased.

In cyclic Voltammetry, the product of concentration has been shown near the electrode surface at the forward scan. When the scan is reversed, the reduced product is oxidized back to starting condition.

Redox reactions whose peaks are shifted apart by increase scan rate are quasi-reversible.

Analysis of the redox reaction peaks is based on the relative heights of the anodic and cathodic current peaks which, illustrated from rate constant, are important for further evaluation and discussion.

Electrochemical behavior of ZrOCl_2 in KF solution:

One reduction peak was observed at approximately ~ -0.3 V corresponding to the reduction consuming 4 electrons as given by an equation.



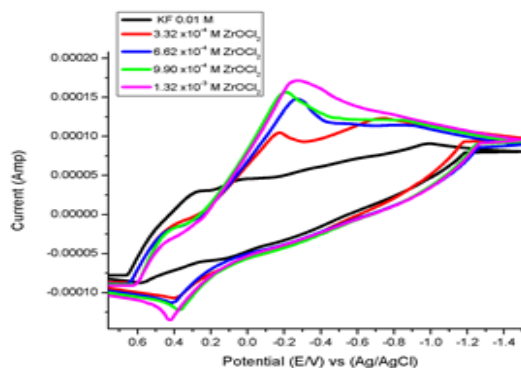
On using a small concentration of ZrOCl_2 , the reduction process took place by two steps, which are observable in Figure 1 and 2 by the two split waves. It can also be noted that 2 electrons were consumed in each reduction step.

Increasing the concentration of ZrOCl_2 was followed by the shift in the reduction wave indicating more solvation process.

Table 1. Effect of conc. of ZrOCl_2 M at 298.15 K, scan rate 0.1

$[\text{M}] \times 10^3$	$(-)\text{E}_{p,c}$	$\text{I}_{p,c} \times 10^5$	$\text{D}_c \times 10^{10}$
0.332	0.162	6.23	6.16
0.662	0.253	7.83	2.45
0.990	0.178	12.1	2.63
1.32	0.226	12.2	1.51

Figure 1. Effect of concentration of zirconyl chloride in 0.1M KF.



The oxidation peak for $ZrOCl_2$ was appeared at ~ 0.4 indicating the reverse direction of the reduction process which is the oxidation of the reduced compound giving 4 electrons. That is to say, four electrons are consumed in the oxidation process.

Effect of scan rate:

The effect of scan rate was made using 1.32×10^{-3} M $ZrOCl_2$ in 0.1 M KF at 298.15 K. The different scans which are used are 0.01, 0.02 and 0.1 V/sec. Table (2) includes the scan rate data for the used $ZrOCl_2$.

E_{pc} , $I_{p,c}$, D_c solvation parameters were also cited in Tables 3 and 4 indicating that more solvation parameters are obtained by increasing the concentration of the zirconyl chloride.

Drawing the relation between $i_{p,c}$ and $v^{1/2}$, straight line was clearly obtained in Figure 3 indicating that the reduction process is diffusion controlled.

Table 2. Effect of scan rate at 1.32×10^{-3} M of $ZrOCl_2$ M at 298.15K

Scan rate	(-) $E_{p,c}$	$I_{p,c} \times 10^4$	$D_c \times 10^{10}$
0.1	0.226	1.22	1.5129
0.02	0.123	0.868	3.81
0.01	0.056	0.708	5.0693

Figure 2. Different scan rates.

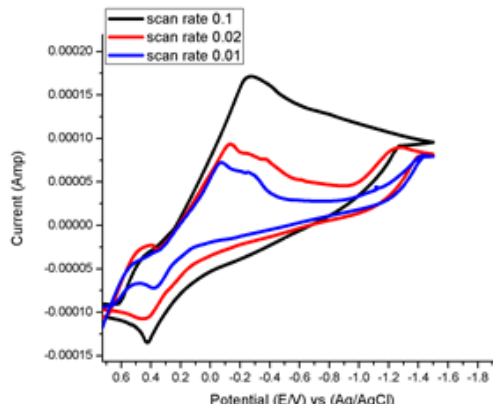
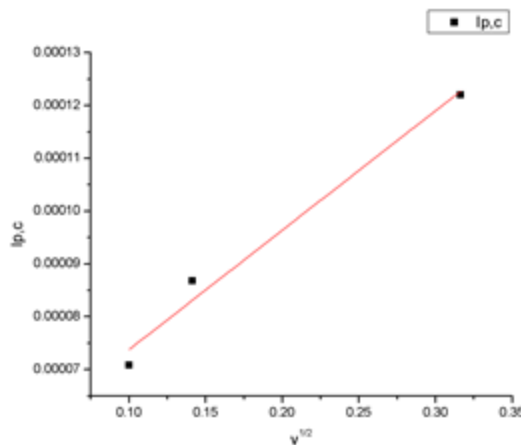
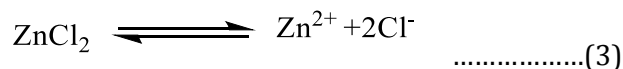


Figure 3. log i_p against $v^{1/2}$



Knowing that zirconium in solution. Knowing that some zirconium salts dissolve in solutions. Trivalent and divalent zirconium have been reported in vapor phase reactions. Zirconium compounds are hydrated and cannot be regarded as a neutral solution. It is a true compound and ionizes according to the following reaction.



ZrO⁺⁺ is the main species in aqueous solutions over range of concentration.

Solutions of zirconyl chloride reach their maximum hydrolysis in three hours [7-10].

Table 3. Cyclic voltammetry parameters for the effect of zirconyl concentrations.

[M] x 10 ³	(-) Ep,c	Ip,c x 10 ⁵	n	Dc ^{1/2} x 10 ⁵	Da ^{1/2} x 10 ¹⁰
0.332	0.162	6.23	2	2.48	6.16
0.662	0.253	7.83	2	1.57	2.45
0.99	0.178	12.1	2	1.62	2.63

1.32	0.226	12.2	2	1.23	1.51
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Table 4. Cyclic voltammetry parameters for the scan rates effect.

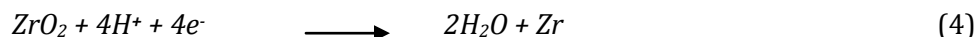
v	$[M] \times 10^3$	$(-) E_{p,c}$	$I_{p,c} \times 10^5$	n	$Da^{1/2} \times 10^5$	$Da^{1/2} \times 10^{10}$
0.1	1.32	0.226	6.23	2	1.23	1.513
0.02	1.32	0.123	7.83	2	1.95	3.810
0.01	1.32	0.056	12.1	2	2.25	5.069

In 1905 Ruer [7] found that the conductivity of zirconyl chloride changes with time showing hydrolysis to be a highly complicated reaction.

Pauli and Adolf [8-10] logically concluded that simple ionization of zirconyl chloride in aqueous solutions and its properties were governed by hydrolysis and complex ion formation. They postulated the existence of a variety of polymeric ions.

They discounted the possibility of $Zr(OH)^{3+}$ existing as a hydrolysis product and eliminated it from their discussion. Laubengayer and Eoten [10] arrived at the conclusion that an average of three hydroxyl ions was associated with each zirconium. All zirconium in solutions was present as ionic species and none was colloidal because of the fact that voltammograms were founded on silver working electrode (SWE).

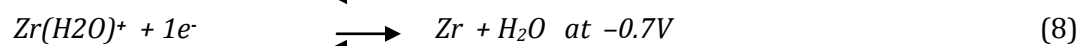
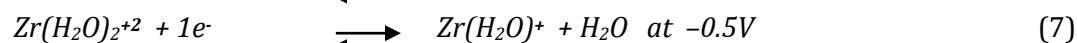
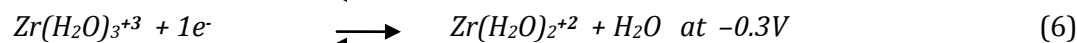
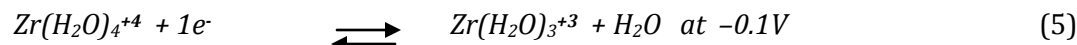
ZrO_2 dissolved in succinic acid solution as ligand [10,11].



Nanotube zirconia and nanoporous has great potential applications in the fields of adsorption, heterogeneous, catalysts, chemical sensors, separation, electronics, optics, biomedical, implants and magnetic [12,13]. The superior mechanical properties, high dielectric constant, chemical stability, electrical and wide band gap of ZrO_2 are the main reasons for applications in electronics, magneto-electronics optics and optoelectronic.

ZrO_2 can be also prepared from zirconyl chloride by heating [13].

It was observed that at low zirconyl ion concentration two hydrated ions are detected in the reduction processes, these may indicate the reduction of $Zr(OH)^{+3}$ and $Zr(OH)_2^{+2}$ ions at $\sim 0.2V$ and $\sim -0.3V$ as shown in Figure 2.



The solubility of Zr due to the formation of $Zr(OH)_5^-$ or $Zr(OH)_6^{2-}$ has been observed [14, 15].

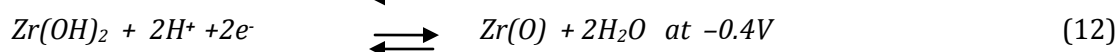
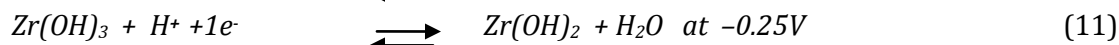
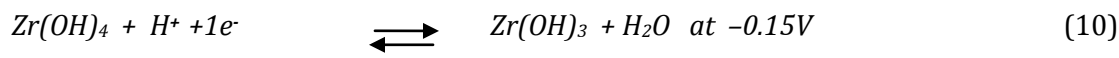
The solubility of $ZrOCl_2$ by addition of Ca^{2+} in alkaline medium ions is due to the reaction cited in Ref 14.



High solubilities of zirconium (IV) and thorium (IV) hydrated oxides in alkaline $CaCl_2$ solutions. The dominant aqueous complexes $Ca_3[Zr(OH)_6]^{4+}$ and $Ca_3 [Th(OH)_8]^{4+}$. The number of OH^- groups were identified and detected [15].

Scan rate 0.02 gave three cyclic peaks for $ZrCl_2$ at -0.15 , -0.25 , -0.4 V, may be corresponding to the reduction processes as follows :

At scan rate 0.02 V/sec



These mechanisms suggested that mechanisms may explain the different small peaks which appear in the reduction process for $ZrOCl_2$ in 0.1M KF solution.

Conclusion

Zirconyl chloride hydrolyzed in 0.1MKF solutions gave an average of three hydroxyl ions associated with zirconium ions. They are $Zr(OH)_4$, $Zr(OH)_3$ and $Zr(OH)_2$. All hydrolyzed ions are found in solutions as ions species and not as colloidal because of the fact that voltammograms were found on using silver working electrode (SWE).

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