ESTABLISHMENT AND VERIFICATION OF MATHEMATICAL MODEL FOR CURRENT LEAKAGE IN BIPOLAR MULTI-COMPARTMENT CELL①

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ABSTRACT A systematical study of current leakage in bipolar multi-cmpartment cell has been made. By using basic conceptions in electrochemistry and establishing equivalent circuit, a reasonable mathematical model of current leakage was developed. After simplified properly, basic principles of current leakage in bipolar electrolytic cells were found out. To verify the model, a series of experiments in electrolysis of aqueous copper sulphate were made. The effects of some elements on current leakage were observed and the mathematical model was verified by comparing the experimental results with the calculated ones according to the model.

Key words: bipolar multi -compartment cell current leakage equivalent circuit mathematical model model verification

1 INTRODUCTION

Compared with monopolar cells, bipolar multi-compartment cells have some advantages such as high electric energy efficiency, large yields/area ratio and low labour strength. In 1970's, Aluminium Company of America succeeded in "Alcoa Electrolysis" using bipolar multi-compartment cells, which stimulated people to do more research on bipolar multi-compartment cells. The efforts of developing inert electrode materials and inert lining materials have been made for many years in order to make the bipolar multi-compartment cells, the ideal cells, for practical use in aluminium reduction[1,2].

Bipolar multi-compartment cells have important energy saving potential not only in aluminium electrolysis, but also in the electrolysis of magnesium, titanium, zinc and superchlorinates. It is known that electric energy efficiency of a cell is the product of voltage efficiency and current efficiency. Due to shortened anode-cathode distance(ACD), lessened bus bars, tabs and other intercell connections, the voltage efficiency in bipolar multi-compartment cells is much higher than that in monopolar cells; but the current efficiency is always lower because of the existence of current leakage. So one of the key problems with designing bipolar multi-compartment cells is to minimize the current leakage.

Until now, most of the authors have just calculated the current leakage when polarization in bipolar multi-compartment cell is linear, and only then can electrolytical cell be simplified into equivalent electric resistance independent of electrolytic current. But in fact no electrolysis can proceed under linear polarization close to equilibrium, so those models about current leakage have great limitation. Although several other authors involved in nonlinear polarization, they could not get the analytical solution of current leakage, and the physical models they used were also defective. Zhao G W *et al*[3,4] solved the problems in a bettter manner. They took the cell voltages obtained from the experiments as known

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ones, which solved the nonlinear relationship between interface of ionic conductors and electronic ones, then solved the triangular equation using matrix method and differential calculus method respectively, and did experiment verification for the first time. But their physical model was still uncompleted .

In this paper, we started from basic electrochemical conceptions and established complete physical model (including resistance of bipolar plate and its polarization of both sides), hoping to describe the current leakage systematically and found out its basic principles to supply the basis for excellent design of bioplar multi-compartment cells. The principles were verified in bipolar multi-compartment cells through electrolysis of aqueous copper sulphate.

2 PHYSICAL MODEL AND EQUIVALENT CIRCUIT

First, two-compartment cell that has one bipolar plate (Fig. 1) is considered. Suppose electrolytic current is constant and the whole electrochemical system is in steady state.

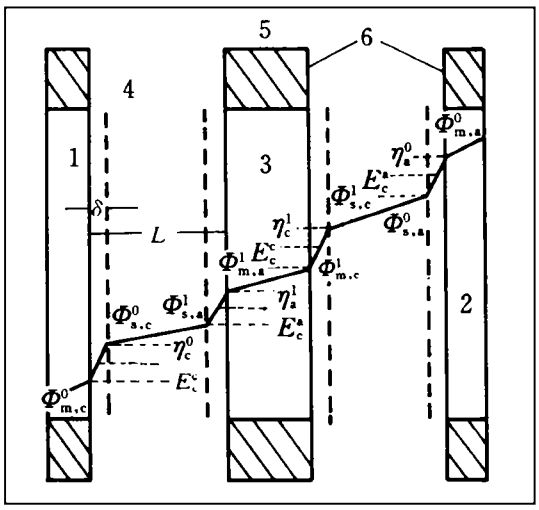

Fig. 1 Sketch of bipolar two-compartment cell

(supposing $\delta \to 0$); 1—cathode; 2—anode; 3—bipolar plate; 4—bypass channel; 5—side channel; 6—insulating material

On the basic electrochemical principles[5], following equations can be given to the same reference electrode:

$$\Phi^1_{m,a} - \Phi^1_{s,a}|_{I_1} = E^a_e + \eta^1_a = U^1_a \quad (1)$$

$$\Phi^1_{m,c} - \Phi^1_{s,c}|_{I_1} = \eta^1_c - E^c_e = U^1_c \quad (2)$$

$$\Phi^1_{m,c} - \Phi^1_{m,a}|_{I_1} = I_1 \cdot R_{BE} \quad (3)$$

$$E^a_e - E^c_e = V_0 \quad (4)$$

where V_0 means theoretical decomposition voltage or equilibrium electromotive force (emf) of the whole battery reaction in the cell; $\Phi^1_{m,a}$ means inner potential in electric double layer at the anodic side of bipolar plate; $\Phi^1_{s,a}$ means inner potential in electrolyte of electric double layer close to the anodic side of bipolar plate. For the same reason, $\Phi^1_{m,c}$ and $\Phi^1_{s,c}$ mean inner potential in electric double layer at the cathodic side of bipolar plate and that in electrolyte close to the cathodic side of bipolar plate respectively; E^a_e and E^c_e mean the equilibrium electrode potential of anode and cathode respectively.

So Fig. 1 can be simplified into the equivalent circuit shown in Fig. 2. Being obtained from basic electrochemical principles, in which η^1_a and η^1_c include concentration polarization and electrochemical polarization, etc., the equivalent circuit is more practical and universal. Popularized to bipolar n-compartment cell, Fig. 2 is changed into Fig. 3.

3 DEDUCTION AND DISCUSSION

In the Kth network, according to Kirchhoff Current Law, there is following equation for the $(K+1)$ th knot in bypass channel:

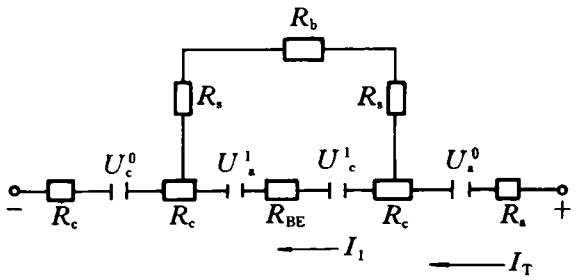

Fig. 2 Equivalent circuit of bipolar two-compartment cell

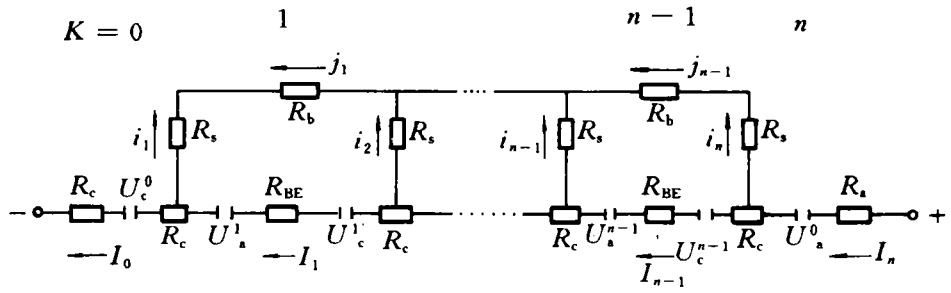

Fig. 3 Equivalent circuit of bipolar n -compartment cell

R_c —resistance of terminal cathode; U_c^0 —potential of terminal cathode; R_a —resistance of terminal anode; U_a^0 —potential of terminal anode; R_{BE} —resistance of bipolar plate; I_K —current through the Kth bipolar plate; n —total number of compartments in bipolar cell; K —ordinal number of the Kth bipolar plate; R_e —resistance of electrolyte in each compartment; R_s —resistance of electrolyte in bypass channel; R_b —resistance of electrolyte in side channel; j_K —current leakage of the Kth bipolar plate; $U_c^K = \eta_c^K - E_e^c$ —cathodic potential of the Kth bipolar plate; $U_a^K = \eta_a^K + E_e^a$ —anodic potential of the Kth bipolar plate.

$$j_{K+1} - j_K + i_{K+1} = 0 \tag{5}$$

For the one in main channel, there is:

$$I_{K+1} - I_K - i_{K+1} = 0 \tag{6}$$

According to Kirchhoff Voltage Law, in network where the Kth bipolar plate exists, the following equations can be given:

$$U_a^K + U_c^K + I_K(R_e + R_{BE}) - j_K R_b - (i_{K+1} - i_K)R_s = 0 \tag{7}$$

$$U_a^K + U_c^K = E_e^a - E_e^c + \eta_a^K + \eta_c^K = V_0 + \eta_a^K + \eta_c^K \tag{8}$$

Boundery conditions are:

$$j_0 = j_n = 0 \tag{9}$$

$$I_0 = I_n = i_1 + I_1 = j_1 + I_1 \tag{10}$$

By means of boundery conditions and equation (6), the following equations can be obtained:

$$I_K = I_0 - j_K \tag{11}$$

Equation (11) shows that current flowing through bipolar plate plus current leakage equals electrolytic current.

3.1 *Limit Condition When Current All Leaks in Bipolar Multi-Compartment Cell*

That is $i_0 = j_K (1 \leqslant K < n)$, then

$$\eta_a^K = 0,\ \eta_c^K = 0,\ I_K = 0 \quad (1 \leqslant K < n)$$

$$i_{K+1} = j_{K+1} - j_K = I_0 - I_0 \quad (1 \leqslant K < n)$$

Substitute them into equation (7) and rearrange:

$$V_0 = I_0(R_b + R_s) \tag{12}$$

Then the following criterion can be obtained:

When $I_0(R_b + R_s) \leqslant V_0$, current all leaks out, and there is no current flowing through bipolar plate;

When $I_0(R_b + R_s) > V_0$, current flows through bipolar plate with existence of partial current leakage.

3.2 *Several Conditions Corresponding to Different Kinds of Polarization When $I_K \neq 0$*

In electrolysis, cathode and anode can be polarized in different manner, such as electrochemical polarization, concentration polarization, Ohm polarization, electric crystallization polarization, monophase or multiphase polarization, etc. Different kinds of polarization result in different forms of equation (7).

3.2.1 A Special Condition When $R_s = 0$

When there is no bypass channel, i. e. bypass resistance is zero, equation (7) becomes:

$$V_0 + \eta_a^K + \eta_c^K + I_K(R_e + R_{BE}) - j_K R_b = 0$$

Substitute it into equation (11) and rearrange:

$$j_K = [V_0 + \eta_a^K + \eta_c^K + I_0(R_e + R_{BE})] \div (R_b + R_e + R_{BE}) \tag{13}$$

Let $E'_K = V_0 + \eta_a^K + \eta_c^K$, while back electromotive force of the Kth compartment is $E_K = V_0 + \eta_c^{K-1} + \eta_a^K$. When $I_K \approx I_{K-1}$ (only when they differ from each other by less than ten

times, and cathodic over-voltage is small in metal deposition), $\eta_c^{K-1} \approx \eta_c^K$ is basically tenable to neighbouring compartments. So $E'_K \approx E_K$, then current leakage round the Kth bipolar plate is:

$$j_K = [E_K + I_0(R_e + R_{BE})] \div (R_b + R_e + R_{BE}) \quad (14)$$

Equation (14) shows that current leakage round the Kth bipolar plate can be obtained by measuring back emf of the cell.

Let $U'_K = V_0 + \eta_a^K + \eta_c^K + I_K(R_e + R_{BE})$, and voltage of the Kth compartment is $U_K = V_0 + \eta_a^K + \eta_c^K + 0.5I_K(R_e + R_{BE}) + 0.5I_{K-1}(R_e + R_{BE})$. For the same reason, $I_K \approx I_{K-1}$, $\eta_c^{K-1} \approx \eta_c^K$, so $U_K \approx U'_K$, then current leakage round bipolar plate is:

$$j_K = U_K/R_b \quad (15)$$

Equation (15) shows that current leakage round the Kth bipolar plate can be obtained by measuring voltage and side resistance of the compartment.

3.2.2 General Conditions When $R_s \neq 0$

(1) Current leakage for linear polarization

Suppose anode and cathode are in weak polarization, then there is a linear relationship between over-voltage and current:

$$\eta_a^K + \eta_c^K = I_K R_r \quad (16)$$

where R_r is the resistance of total electrolytic reaction and is independent of I_K.

Substitute equation (16) into equations (4), (7), (11) and rearrange:

$$R_s j_{K+1} - (R_b + 2R_s + R)j_K + R_s j_{K-1} = -U_0 \quad (17)$$

where $R = R_r + R_e + R_{BE}$; $U_0 = V_0 + I_0 R$

U_0 may be thought as the supposed monopolar cell voltage in linear polarization with current I_0, which can calculated from theoretical decompostion voltage, equivalent resistance of the total electrolytic reaction, resistance of bipolar plate and resistance of electrolyte.

Equation (17) can be solved by methods of differential calculus and matrix.

(2) Current leakage for nonlinear polarization

When one or both of the electrodes in each compartment is strongly polarized, there are nonlinear terms in equation (7), so current leakage can't be calculated in linear polarization manner. If the relations between over-voltage and current in both reactions on bipolar plate's anodic and cathodic sides were known, current leakage would be calculated by computer. Generally it is difficult to get that relation, so it will be simplified to further step.

Let the first three terms of equation (7) be replaced by U'_K, that is:

$$U'_K = V_0 + \eta_c^K + \eta_a^K + I_K R_e + I_K R_{BE} \quad (18)$$

Cell voltage of the Kth compartment is:

$$U_K = V_0 + \eta_a^K + \eta_c^{K-1} + 0.5I_K(R_e + R_{BE}) + 0.5I_{K-1}(R_e + R_{BE}) \quad (19)$$

when $I_K \approx I_{K-1}$, $\eta_c^K \approx \eta_c^{K-1}$, then

$$U'_K = U_K \quad (20)$$

Usually when bipolar electrolytic resistance can be ignored and total current leakage is small, neighbouring compartments have almost the same current leakage and cathodic polarization in metal deposition is weak, so equation (20) is tenable.

The following equation[4] can be deduced from equation (20):

$$R_s j_{K+1} - (2R_s + R_b)j_K + R_s j_{K-1} = -U_K \quad (21)$$

It can be seen that equation (21) is only a special illustration and can not be used universally.

4 MODEL VERIFICATION

4.1 *Experiment Principles*

To verify the conclusions deduced above experiment for electrolysis of aqueous copper sulphate with constant current was carried out in bipolar multi-compartment cell. Metals depositing on terminal cathode and each cathodic side of bipolar plates were determined by chemical analysis. If Faraday current through terminal cathode and the Kth bipolar plate are I_0 and I_K ($K = 1, 2, \cdots, n-1$) respectively, the current efficiency of them can be given as:

$$\eta_{CE}^0 = W_0/(qI_0t), \quad \eta_{CE}^K = W_K/(qI_Kt)$$

where $K = 1, 2, \cdots, n-1$; q means electrochemical equivalent of metals depositing on cathodes.

Because terminal cathode and each bipolar plate are almost in the same environment, current loss efficiency and current efficiency are almost the same.

So $\eta_{CE}^{0} = \eta_{CE}^{K}$

And $I_K = W_K I_0 / W_0$

Then current leakage round the Kth bipolar plate is:

$$j_K = I_0 - I_K = (1 - W_K/W_0) I_0 = \varepsilon_K I_0$$

where $\varepsilon_K = 1 - W_K/W_0$ is called current leakage coefficient.

4.2 *Experimental*

Bipolar cell was designed as a rectangle. The dimensions of cell and plate were measured by a 0.02 grade vernier caliper. Electrodes with sides insulated by AB glue were made from high-strength graphite. The electrolyte was made up of 200 g/L $CuSO_4 \cdot 5H_2O$, 30 mL/L sulphuric acid and 12 g/L $KAl(SO_4)_2 \cdot 12H_2O$, which were all prepared with analytical reagents and distilled water.

Constant current was supplied by model JWL-30 constant-current DC power supplier. Current and cell voltage were observed from model 7150 6-1/2 digit multimeter combined with a 0.02 grade, 0.1 Ω standard resistance box. Electric conductivity of aqueous solution was determined by model DDS-12 electric conductivity meter. After electrolysis, deposited copper was first washed by water, immerged into distilled water and absolute alcohol for several minutes respectively, and then dissolved in 1:1 HCl + 33% H_2O_2 in beaker. After dissolution completed, pulled the plate out, heated the beaker to expel H_2O_2, then cooled it down. Finally the quantity of deposited copper was chemically analyzed.

4.3 *Results and Discussion*

4.3.1 Effect of Electrolytic Current on Current Leakage

With unchanged geometrical dimensions of cell and electrodes, constant composition and flowing velocity of electrolyte, effect of electrolytic current I_0 on current leakage can be observed. As shown in Fig. 4, current leakage coefficient ε_K goes down quickly with increasing electrolytic current, meaning that electrolytic current has great influence on current leakage. It can be seen in experiment that when electrolytic current was less than a certain value, there would be no metal depositing on bipolar plates, i.e. the current all leaked out. This can be explained as follows. There are two current flowing channels in bipolar multi-compartment cell: one is the bypass channel where conductors are all ions, and only back emf between terminal cathode and anode needs to be overcome; the other is the channel through bipolar plate where current must flow through the interface between ionic conductor and electronic conductor, i.e. overcome back emf between the two sides of bipolar plate other than that between terminal electrodes. When electrolytic current is small, the voltage between two terminal plates of bipolar multi-compartment cell is small, so it is easier for current to flow through the bypass channel. While the current is large, voltage is large too, back emf can be overcome, and ε_K is small. This also verifies the criterion mentioned above reasonable.

4.3.2 Effect of Electrode Area on Current Leakage

Fig. 5 shows that ε_K decreases quickly

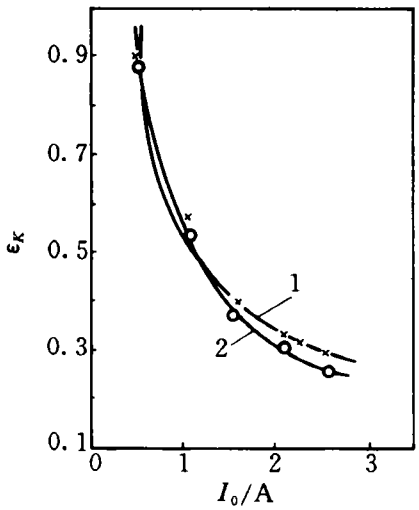

Fig. 4 Effect of I_0 on ε_K in three-unit cell

1—upper bipolar plate ($K = 2$);
2—lower bipolar plate ($K = 1$)

increasing electrode area. The reason is that resistance of side channel of multi-compartment cell increases obviously with increasing electrode area, and this makes ε_K decrease. When electrode area is smaller than the cell by 70%, ε_K will be above 95%. Here the criterion mentioned above is verified once again.

4. 3. 3 Effect of Flowing Velocity of Electrolyte on Current Leakage

As shown in Fig. 6, when flowing velocity of electrolyte increases, ε_K rises up at the begining and then becomes stable. It is because flowing electrolyte makes ions in bypass channel move more quickly and speeds up the electronic migration, which leads to increasing current leakage. But increasing flowing velocity also decreases polarization of concentration difference on bipolar plates, and makes the ve become gradually even.

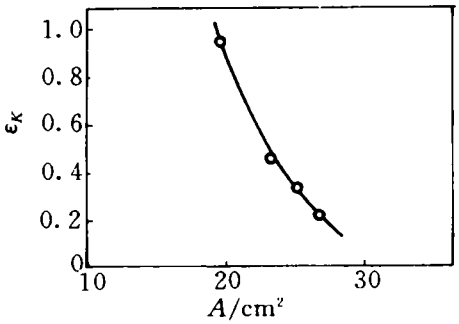

Fig. 5 Effect of electrode area A on ε_K in bipolar two-compartment cell

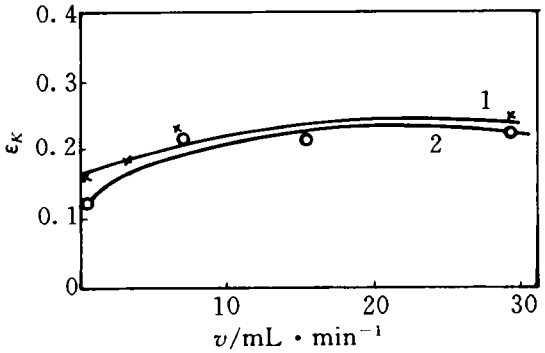

Fig. 6 Effect of electrolyte flowing velocity v on ε_K in bipolar three-compartment cell

1—upper bipolar plate($K = 2$);
2—lower bipolar plate($K = 1$)

4. 3. 4 Verification of Mathematical Model

Mathematical model for current leakage calculation by both back emf method and cell voltage method is verified through a series of experimental data. Experimental conditions and data are shown in Table 1. Current leakage measured by experiments and that calculated from the model are shown in Table 2.

It can be seen from Table 2 that measured current leakage accords basically with calculated one from the model (errors result from assumptions in deduction, equivalent circuit itself and experiment), showing that mathematical model deduced in this paper is basically correct.

5 CONCLUSIONS

(1) Bipolar multi-compartment cell is made up of terminal anode, terminal cathodes and bipolar plates. It is a complicated cell system that has channels for electrolyte circulat-

Table 1 Experiment conditions and data

n	Experimental conditions	I_0 /A	K	Cell voltage/V	Back emf /V
4	$R_s = 0$ $R_b = 6.47\ \Omega$ $d_{a,c} = 1.5$ cm $d_{BE} = 2.0$ cm $R_e = 0.363\ \Omega$ $R_{BE} = 0$ $\sigma = 9.2\times10^{-2}$ $\Omega^{-1}\cdot cm^{-1}$ $T = 20$ C	2.0	1 2 3 4	2.100 2.010 1.980 2.350	1.600 1.560 1.520 1.550
2	$R_s = 0$ $R_b = 6.84\ \Omega$ $R_e = 0.384\ \Omega$ $R_{BE} = 0$ $d_{a,c} = 2.0$ cm $d_{BE} = 2.0$ cm $\sigma = 8.6\times10^{-2}$ $\Omega^{-1}\cdot cm^{-1}$ $T = 28$ C	2.5 2.0 1.5	1 2 1 2 1 2	2.392 2.252 2.400 2.201 2.098 1.873	1.470 1.495 1.473 1.430 1.405 1.370

Notes: n —total number of compartments; K —ordinal number of compartments; $d_{a,c}$ —anode-cathode distance; d_{BE} —thickness of bipolar plate; σ specific conductivity; T —room temperature.

Table 2 Current leakage measured and calculated

n	Electrolytic current I_0 /A	Ordinal number of bipolar plate	Calculated results/A		Measured results	
			Cell voltage method	Back emf method	ε_K %	Current leakage /A
4	2.0	1	0.328	0.340	19.5	0.390
		2	0.314	0.330	19.0	0.380
		3	0.309	0.329	19.2	0.384
2	2.5	1	0.349	0.336	13.0	0.325
	2.0	1	0.352	0.310	16.4	0.328
	1.5	1	0.307	0.274	21.0	0.315

ing and gas, metal removing. There certainly exists current leakage because of its special properties such as bypass channel, side channel and no bus connections in bipolar plate, etc. So it is important to find out the principles of current leakage for optimum design of bipolar multi-compartment cell.

(2) It is found through calculation that there is no current flowing through the bipolar plate if electrolytic current and resistance of bypass channel are small enough. When $I_0(R_b + R_s) \leqslant V_0$, current leaks out completely; when $I_0(R + R_s) > V_0$, current leaks out partially.

(3) The model for equivalent circuit deduced from basic electrochemical conceptions gives a good illustration of current leakage in various states and conditions. Calculating formula is obtained by solving equations in finite element difference method with consideration of bent electric force lines. When $R_s = 0$, i.e. there is no bypass channel in bipolar cell, current leakage can be described in back emf method (equation (14)) and cell voltage method(equation(15)) respectively.

(4) Principles of current leakage measurement in aqueous bipolar cell is described. Effect of electrode area, electrolytic current and flowing velocity of electrolyte on current leakage are studied through electrolysis of aqueous copper sulphate.

(5) Mathematical model for current leakage deduced from electrochemical conceptions is verified by electrolysis of aqueous copper sulphate in bipolar two-compartment cell and four-compartment cell respectively. Calculated values are in good agreement with experimental ones.

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