

EFFICIENCIES OF BIPOLAR CELLS

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ABSTRACT There is a great potential of energy saving in bipolar cells. Based on research for several years, a theoretical analysis of energy saving in bipolar cells is given, and some practical data presented.

KEY WORDS bipolar cells, energy saving , theoretical analysis

THE most attractive point of bipolar cells is their great potential of energy saving. 30 % or more of DC electricity can be saved if the molten salt electrolysis for Mg, Al, Pb, and Zn in bipolar cells designed correctly is substituted for a conventional cell.

If some pieces of electron conducting plates are inserted between the anode and cathode of a conventional cell, they would become bipolar electrodes. The side of the plates facing the anode would become cathodic and the opposite side anodic , as the current is passing through the plates.

If n bipolar electrodes are added into a cell, n additional compartments would be established. These compartments of a bipolar cell function as conventional cells in series, but this state is formed directly as the current is passing through the bipolar electrodes. No connections are required among the bipolar electrodes themselves, and between the bipolar electrodes and the power supply.

It makes no difference in principle of electrolysis between bipolar and monopolar cells. The difference between them is the ways of connection and arrangement of the electrodes. However, the very difference in structure between the two kinds of cells gives bipolar cells a possibility of a great increase in power efficiency.

The main advantages of bipolar cells are : (1) High voltage efficiency. (2) High power efficiency for a correctly designed bipolar cell. (3) Low capital investment because of the combination of low investment in rectifiers, bus bars etc. and high productivity of bipolar cells. (4) Considerable improvements of the environments and the recovery of the anodic gas etc.

1 POWER EFFICIENCY

The power efficiency of a cell (η_p) is the product of voltage efficiency (η_v) and current efficiency (η_i), that is

$$\eta_p = \eta_c \times \eta_i$$

In molten salt electrolysis for Al, Mg, Pb and Zn from their chlorides, the current efficiencies are usually high. For example, a current efficiency of 90 % was reached for Al ^[1], and 85 % ~ 90 % for Mg. In the lab experiments of molten salt electrolysis for Pb and Zn, even 96 pct of current efficiency could be reached ^[2, 3]. The same level of current efficiency could be obtained in the experiments of pilot scale ^[4, 5]. These results showed that the further improvements of the current efficiency for above processes would be rather difficult. On the contrary, the voltage efficiency of molten salt electrolysis in monopolar cells are very low, usually lower than 50 %. It is evident that there is a great room left for the improvement of voltage efficiency, in which bipolar cells happen to take an important part. Here we use the word potential to emphasize that an improvement in voltage efficiency is not equivalent to a higher power efficiency because there is a spontaneous trend for the current to bypass the bipolar electrodes in a bipolar cell. So the current efficiency of a bipolar cell is always lower than that of a monopolar cell. Therefore to increase the voltage efficiency of a bipolar cell is the key to realise the energy saving, the difficult problem to be solved is how to keep the current efficiency of a bipolar cell not too low in order to ensure a high power efficiency of a bipolar cell.

2 VOLTAGE EFFICIENCY

2.1 THE IR DROPS IN BIPOLAR ELECTRODES

The IR drops in bipolar electrodes are very small compared with those in monopolar electrodes. Fig.1 shows a piece of electrode used either as a bipolar or monopolar electrode. It is assumed that no matter how it is used, it will be immersed into the same deepness of the electrolyte, whose surface is ABCD (see Fig. 1), and thus in both cases this electrode has the same reacting area. For the same electrolytic process, the currents I_m and I_b , flowing through the monopolar and bipolar electrodes respectively, should be equal each other in magnitude but different in direction. I_m flows along the direction normal to the cross-section ABCD, i.e. from the upper end to the lower end of the electrode through the cross-section area, $A_{cm} = A_{ABCD}$, and the distance $L_{cm} = L_{GA} + L_{BF}/2$, if it is assumed that the current distribution is homogeneous along vertical direction. I_b flows along the direction normal to the plane BCEF through the cross-section area, $A_{cb} = A_{BCEF}$ and the distance $L_{cb} = L_{AB}$. In the commercial scale they can be evaluated as follows. $L_{cb} \approx [1/(6 \sim 8)] \times L_{cm}$, $A_{cb} \approx (3 \sim 4) \times A_{cm}$. Because the resistance of a conductor is directly proportional to its length and reversely proportional to its cross-section, the IR drop of a bipolar electrode is only $[1/(18 \sim 32)]$ of that of a monopolar one and should be in the range of 20 ~ 50 mV.

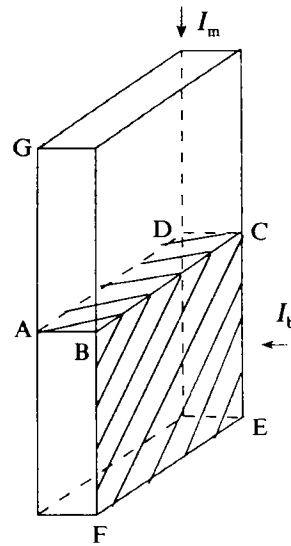


Fig. 1 The directions of current and IR drops of mono- and bi-polar electrodes

3.2 VOLTAGE EFFICIENCY OF BIPOLAR CELLS

There are n compartments in a cell with $n-1$ bipolar electrodes. The average cell voltage for each compartment is given by

$$(1/n) \sum_{k=1}^n U_k = (1/n)(nE_e + \sum_{k=1}^n \eta_{kc} + \sum_{k=1}^n \eta_{ka} + \sum_{k=1}^n U_{ks} + U_c + U_a + U_{cc} + U_{ca} + \sum_{k=1}^{n-1} U_{kb}) \quad (1)$$

where U_k – the cell voltage of the k -th compartment; E_e – the emf of the formation of the electrolyzed compound; η_{kc} and η_{ka} – the overpotential of the cathode and anode of the k -th compartment, respectively; U_{ks} – the IR drop of the electrolyte in the k -th compartment; U_c and U_a – the IR drop in the terminal cathode and anode, respectively; U_{cc} and U_{ca} – the IR drops for the connections of the terminal cathode and anode, respectively; and U_{kb} – the IR drop in the k -th bipolar electrode. These variables vary with the ordinal numbers of the compartment, which is caused by the difference in current leakage in different compartments.

The cell voltage of a monopolar cell is given by

$$U_m = E_e + \eta_c + \eta_a + U_s + U_c + U_a + U_{cc} + U_{ca} \quad (2)$$

The first four terms of the right hand side of equation (1) include the effects of reaction conditions, emf, polarization, resistance of the electrolyte, the dimensions of the cell on the cell voltage, three of them vary with the ordinal numbers of the compartments. Such a variation would not be large in a correctly designed bipolar cell, and the sum of the first four terms would be approximately equal to the first four terms of equation (2), i. e.

$$(nE_e + \sum_{k=1}^n \eta_{kc} + \sum_{k=1}^n \eta_{ka} + \sum_{k=1}^n U_{ks})/n \approx E_e + \eta_c + \eta_a + U_s \quad (3)$$

At normal conditions the value of the left hand side of equation (3) should be a bit smaller than that of the right hand side. When there is no current leakage in a bipolar cell, the terms with subscript k in the left hand side of equation (3) would no longer vary with the ordinal numbers of compartments, the two sides of equation (3) would be equal each other. When current leakage is 100 %, i.e. the current completely bypasses all bipolar electrodes, and the bipolar electrodes would be out of action. Hence, $n=1$, the cell becomes a conventional cell, the two sides of equation (1) are also equal each other.

On the other hand, the left terms in the equations (1) and (2) are related to the IR drops of electrodes themselves and their connections only for each compartment of a bipolar cell and for a monopolar cell, respectively. These IR drops in bipolar cells considerably differ from that in monopolar cells. If the materials for the cathode and anode are the same which is possible for the molten salt electrolysis of Al, Pb and Zn chlorides, then we obtain

$$\sum_{k=1}^{n-1} U_{kb} = (U_c + U_a)/[2 \times (18 \sim 32)] \quad (4)$$

As long as n value is large enough, the average IR drops of electrodes and their connec-

tions for each compartment of a bipolar cell

$$U_{cb} = [U_c + U_a + U_{cc} + U_{ca} + \sum_{k=1}^{n-1} U_{kb}] / n \quad (5)$$

would be very small. For example, if $n=10$, $U_{cb} = (1.2 \sim 1.3) \times (U_{em}/10)$, where $U_{em} = U_c + U_a + U_{cc} + U_{ca}$, is the IR drops of electrodes and their connections for a monopolar cell. For a bipolar cell, the larger the n value, the smaller the mean IR drop of electrodes and their connections and hence the higher the voltage efficiency. However, n can not be too large, because the larger the n value, the larger the current leakage, and the lower the current efficiency. If n is too small, e.g. $n < 5$, the voltage efficiency would not be high enough to make a full use of the potential in energy saving of the bipolar cell.

When a cell is extended, the voltage efficiency of a bipolar cell will be a bit lower, and that of a monopolar cell much lower. The decrease of voltage efficiency is caused by two factors. First, the sum of IR drops in electrodes increases because of the increase of dimensions of the electrodes. For a conventional cell, the increase of the sum of IR drops in cathode and anode can reach $1.0 \sim 1.5$ V. The corresponding value for each compartment of bipolar cells can be evaluated by $(1.2 \sim 1.3) \times (1.0 \sim 1.5) / n$ V. For a extended bipolar cell with 10 compartments, the average increase of IR drops for each compartment would therefore be less than 0.2 V. Second, the reaction zone expands to the place further from the surface of the electrolyte after extending a cell, it would take longer time for the anodic gas to escape out of the electrolyte, increasing the bubble fraction in the electrolyte, hence, increasing the IR drop of the electrolyte. This effect is the same for both bipolar and monopolar cells. In order to minimize this effect, attention must be paid to the electrode design, especially to the electrodes where gas is difficult to escape. For example, an anode with a reaction plane facing down would cause to increase greatly the bubble fraction in the electrolyte and IR drop of the electrolyte.

Bipolar cells play an important part for the improvement of voltage efficiency. The voltage efficiency of molten salt electrolysis is usually less than 50%. For instance, the voltage efficiency of a diaphragm cell for Mg is usually less than 45%, and that of diaphragmless cell for Mg less than 50%, while the voltage efficiency of experiments of a bipolar cell for Mg of commercial scale can reach 72%^[4]. The corresponding values in bipolar cells of molten chloride electrolysis are 72% for Pb, 74% for Zn^[2], 62% for Al^[1].

3 CURRENT EFFICIENCY

3.1 THE SPONTANEOUS TREND OF CURRENT LEAKAGE IN BIPOLAR CELLS

There is an inherent factor which decreases current efficiency in bipolar cells, i.e., the natural trend of bypassing the bipolar electrodes of current. The channel through which the current bypasses one or more bipolar electrodes is called bypass channel, and the one along which the current flows through electrodes and electrolyte and undergoes electricity/chemistry conversion at the electrode/electrolyte interface, is called electrolytic channel.

Comparing equations (1) and (2), equation (1) multiplied by n is the cell voltage of a bipolar cell with n compartments, and can be regarded as the voltage of electrolytic channel, equation (2) is the cell voltage of a conventional cell, and can be taken as the voltage of bypass channel through which the leakage current bypasses all bipolar electrodes. In spite of the magnitude of the leakage current, the voltage of electrolytic channel must be equal to that of bypass channel because these two channels are electrically connected in parallel. In practice, leakage current must be much smaller than the electrolytic current. Multiplied by n , the first three terms in right hand side of equation (1) (i. e. the reaction resistance) are at least n times of corresponding terms of equation (2), and the sum of the 5-th term through the 9-th term of equation (1) (i. e. the electrodes and their connections resistance) is larger than that of the 5-th term through the 8-th term of equation (2). These mean that the resistances both in reaction and in electrodes and their connections of the bypass current are smaller than those of electrolytic current. The reaction resistance decreases $1/n$ when the leakage current bypasses one bipolar electrode; and $(n-1)/n$ when leakage current bypasses all $(n-1)$ bipolar electrodes. It follows from above that there is a spontaneous trend in bipolar cells that parts of current bypasses one or more bipolar electrodes. In order to balance the voltage of electrolytic channel and that of bypass channel, the IR drop of electrolyte of equation (2) must be increased, i.e. the cross-section area decreased, at the limit, the electrolyte between different compartments is isolated, i.e. there is no bypass channel, the resistance of current leakage would be infinite, and the current leakage would approach zero. However, because of the technical requirements for feeding, the collection of the metal produced, the discharge of the slag, and the circulation of the electrolyte etc.^[6]. As well as the absorption of the electrolyte in pored refractory materials linings, the formation of some interconnect domains of electrolyte among various compartments seems to be inevitable, so the current leakage can hardly be eliminated.

As mentioned above, the requirements for energy saving are contrary to those for some technical demands and further study on current leakage must be made.

3.2 THE QUANTITATIVE TREATMENT OF THE CURRENT LEAKAGE IN BIPOLAR CELLS

In order to minimize the current leakage in bipolar cells and in batteries with common electrolyte, some mathematical models have been put forward^[7~11], and the little no much progress has been made since then. An analytical solution of current leakage for non-linear polarization proved to be correct by systematic experimental research is still the one published several years ago^[19], in which the current leakage for linear polarization is given by

$$j_k = U_c / (R_q + R) \{ 1 - \cosh[(k - n/2)b^{1/2}] / \cosh[(n/2)b^{1/2}] \} \quad (6)$$

j_k obtained in this way is not a practical one, but the minimum value of the current leakage at given operating current.

The current leakage for nonlinear polarization, j_k , is given by

$$j_k = (U_k / R_q) \{ 1 - \cosh[(k - n/2)(R_q / R_s)^{1/2}] / \cosh[(n/2)(R_q / R_s)^{1/2}] \} \quad (7)$$

It can be seen from equation (7) that the current leakage is proportional to U_k , and dependent of n , R_s and R_q . For the convenience of application, a further analysis of the influences of various factors on U_k , n , R_s and R_q , hence on current leakage should be made.

(1) The cell voltage of the k -th compartment, U_k , which has the most significant effect on j_k ^[19] and U_k itself is affected by many factors. The factors which make the mean value of U_k larger increase the current leakage, i.e. decrease the average current efficiency, hence increase the power consumption. An increase in average value of U_k also make the power consumption larger directly. The factors which affect U_k are as follows.

(a) The emf for the formation of the electrolyzed compound. The emf is large when the standard free energy of the compound is a large negative value; a component in the electrolyte is playing a part to form a solution with negative deviation from ideality; and the concentration of the compound is low. The emf decreases when the temperature is raised.

(b) Electrode polarization. First, it depends on the properties of the electrolyte system. Electrode polarization is small when the exchange current density and diffusion coefficient are large. The composition of the electrolyte, the concentration of the compound and temperature have effects on the state of the compound in the electrolyte, hence on the polarization. Polarization also depends on the technical conditions, which increases as current density is increased. Materials for electrodes may have a catalytic or inhibitive effect on the reaction.

(c) The IR drop of the electrolyte in every compartment. This IR drop increases with increase of the electrode spacing, the specific resistance of the electrolyte, the current density and the bubble fraction in the electrolyte, and it decreases with increasing of the electricity conducting area of the electrolytic compartments. Anodic gas would increase the IR drop.

(d) The IR drops in the electrodes. As far as the IR drops in the electrodes are concerned, the key points are the specific resistance of the material for a electrode, the length and the cross-section area of a electrode. For a bipolar cell, the number of the bipolar electrodes is also a key point as discussed above.

(e) If increases in R_s and R_q are caused by a smaller bypass channel and manifold, current leakage would become smaller, but cell voltage a bit higher.

(2) The total number of the compartments in a bipolar cell, n ^[19]. The larger the n value, the larger the current leakage, thus n cannot be too large; On the other hand, the smaller the n value, the lower the voltage efficiency, n cannot be too small either. For the synthesis of perchlorides in the aqueous solution, n can reach 50 without the significant reduction of current efficiency^[16]. But for molten salt electrolysis, n can hardly be over 10.

(3) R_s and R_q ^[19]. Generally, an increases in R_s and R_q would make current leakage smaller, and the effect of R_s is more significant than that of R_q . It is very difficult to compromise the requirements between energy saving and other technical demands such as feeding, tapping, etc. Special design which compromise the above contrary requirements must be made on the basis of the whole process and the integral design of the cell with considerations of production capacity, investment and operational cost, labour, materials and energy ratings, etc.

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双极性电解槽的效率

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摘要 双极性电解槽有巨大的节能潜力。根据数年的实验研究, 对双极性电解槽的节能作了理论分析, 并给出一些实验数据。

关键词 双极性电解槽, 节能, 理论分析

中图分类号 TF111.522, TQ151.15