

## A STUDY OF THE DISCHARGE PERFORMANCE OF THE Tl/Fe REDOX FLOW SYSTEM

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(Received September 30, 1983, in revised form December 17, 1983)

### Summary

The anodic polarization phenomenon in a Tl/Fe redox flow battery was studied. By adding a small amount of Pd (0.02 wt %) to the inert graphite electrode in the Tl half cell, the discharge overpotential can be reduced by about 50%.

It was also found, by experimental design, that the discharge output power of our Tl/Fe redox battery was maximized when  $[\text{Fe}^{3+}] = 0.32\text{M}$ ,  $[\text{Tl}^{3+}] = 1.12\text{M}$  and the discharge current density  $i = 13\text{ mA/cm}^2$ .

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### Introduction

The redox flow battery has recently become a potential secondary battery [1 - 10]. Its characteristics are

(1) It is easy to store and transport because the reactant and product are both in the soluble state. Furthermore, its capacity is not limited by the electrodes and it is proportional to the quantity of the reactant.

(2) It uses inert electrodes. During charge/discharge, the electrodes will not be deformed or flake. In principle, the inert electrode can be charged and discharged infinitely.

(3) It has a very high active material utilization because, in general, the liquid reactant and product diffuse much more effectively than the solid reactant and product of most other storage systems.

Because of these advantages, the redox battery is potentially useful in electric power storage.

Until now, the majority of the redox battery systems used a chloride salt as the electrolyte. The most popular ones are Cr(II/III)-Fe(III/II) and Tl(III/IV)-Fe(III/II) systems. However, their low electrode potential and rapid anodic polarization during discharge are the major drawbacks.

This work is a study of the Tl(III/IV)-Fe(III/II) redox flow battery system. Several treatments were used to reduce anodic polarization. The results

were analyzed by the galvanostatic transient method and the optimum discharge condition was also determined statistically

## Experimental

The design of the cell is shown in Fig 1. The cell was made up of two acrylic half cells, each measuring 8 cm × 3 cm × 12 cm. These two half cells were separated by an anionic exchange membrane (Asahi Glass Co.) Two inert graphite electrodes were adjacent to the cell wall and a saturated calomel reference electrode was placed in the center of each of these two half cells to measure the electrode potential and membrane voltage. Various surface treatments were applied to the anode to modify its polarization behavior. Ferric chloride solution and  $TiCl_3$  solution were placed in the cathodic and anodic compartments, respectively. 3N HCl solution was used as supporting electrolyte. The amount of reactant in each half cell was 250 ml.

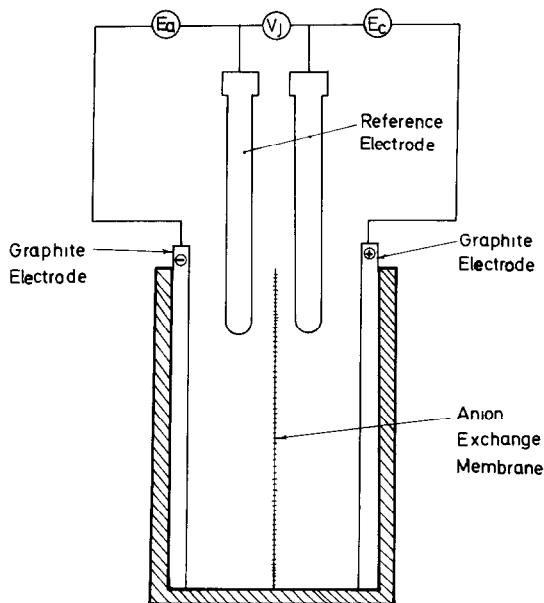


Fig 1 Schematic diagram of the cell  $E_a$ , anode potential,  $E_c$ , cathode potential,  $V_j$ , membrane voltage drop

The galvanostatic transient method was used to analyze the electrode potential. The circuit diagram is shown in Fig 2. A differential amplifier (Tektronix 5103 N with plug-in 5A 22N differential Ampl, 5B 10N Time Base/Ampl) was used to overcome the noise signal due to the  $IR$  resistance between the reference and the working electrodes. Accurate readings of

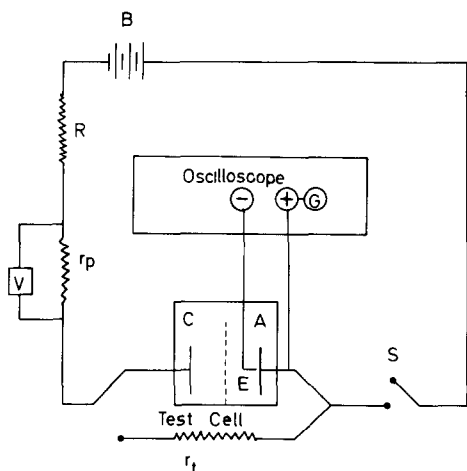
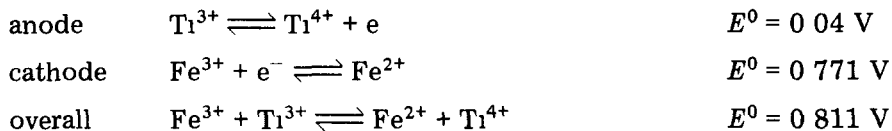


Fig 2 Schematic diagram of the circuit for measuring electrode overpotential A, anode of redox cell, C, cathode of redox cell, E, reference electrode, B, 12 V 150 A h lead-acid battery, R, variable resistance panel,  $r_p$ , 1 ohm precision resistor, S, switch,  $r_t$ , 1 ohm precision test resistor, V, digital voltmeter

ohmic drop, activation overpotential, and concentration overpotential were recorded on an oscilloscope and were analyzed

All experimental results were obtained from tests on a single cell and each experiment was repeated three times with a maximum percentage deviation within 2%

The cell reactions are



## Results and discussion

### 1 The discharge characteristics of the $Ti/Fe$ battery system

Figure 3 shows the discharge characteristics of the  $Ti(III/IV)-Fe(III/II)$  battery system  $V$ ,  $V_j$ ,  $\eta_a$ ,  $\eta_c$  are the results of the first discharge cycle, where  $V$  denotes output voltage,  $V_j$  denotes membrane voltage drop,  $\eta_a$  and  $\eta_c$  denote anodic overpotential and cathodic overpotential, respectively.  $V'$ ,  $V_j'$ ,  $\eta_a'$ ,  $\eta_c'$  are the corresponding results for the second discharge cycle of the same battery. The results of all the subsequent discharge cycles were close to that of the second discharge

According to Fig 3, the output voltage,  $V$ , decreased while the anodic overpotential,  $\eta_a$ , and the cathodic overpotential,  $\eta_c$ , increased as the discharge current density increased. Membrane resistance was minimal but

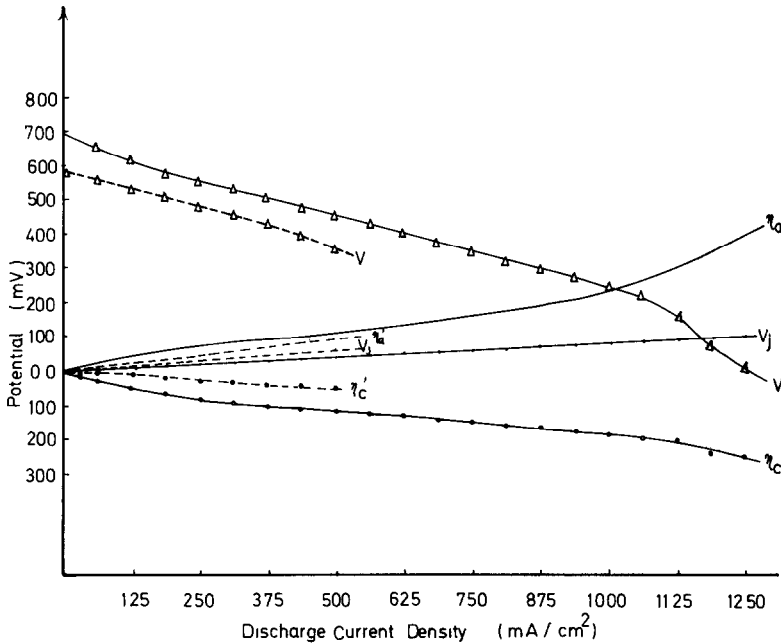


Fig 3 The discharge characteristics of the Ti/Fe system

detectable This is probably due to the obstruction of pores in the membrane by  $\text{Fe}(\text{OH})_3$  [6] Although the system was highly acidic, the pH value at the membrane passage could be quite high Consequently, a residue of amorphous  $\text{Fe}(\text{OH})_3$  precipitate was easily formed If the membrane is rinsed with HCl solution, the initial conductance of the membrane will be recovered

The large increase, about 65 mV, in the cathodic overpotential after the first discharge was probably due to the growth of  $\text{Fe}(\text{OH})_3$  or other oxides on the surface of the graphite electrode The presence of HCl, however, limited the growth of oxides Thus, the cathodic overpotential did not increase on the subsequent discharge cycles Note that the cathodic overpotential is smaller than the anodic overpotential

## 2 The effect of the surface treatment of the anode on the anodic overpotential

One of the major problems of the redox battery is the polarization of the anode, which is much more serious than that of the cathode The graphite electrode in the Ti half cell was treated by various methods in our experiments The impact on the discharge of the battery is shown in Fig 4

Serious anodic polarization was observed (curve  $A_0$ ) if the graphite electrode was rinsed with 3N HCl only When the graphite electrode was treated as in the following steps [4, 5], however, the anodic overpotential was greatly reduced (curve  $A_1$ )

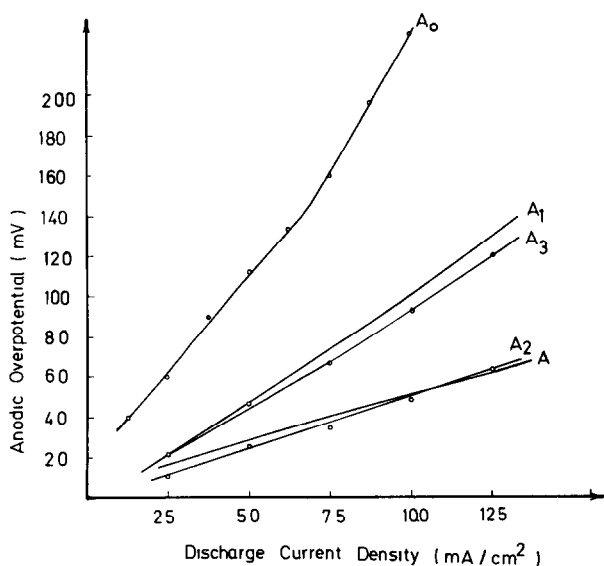
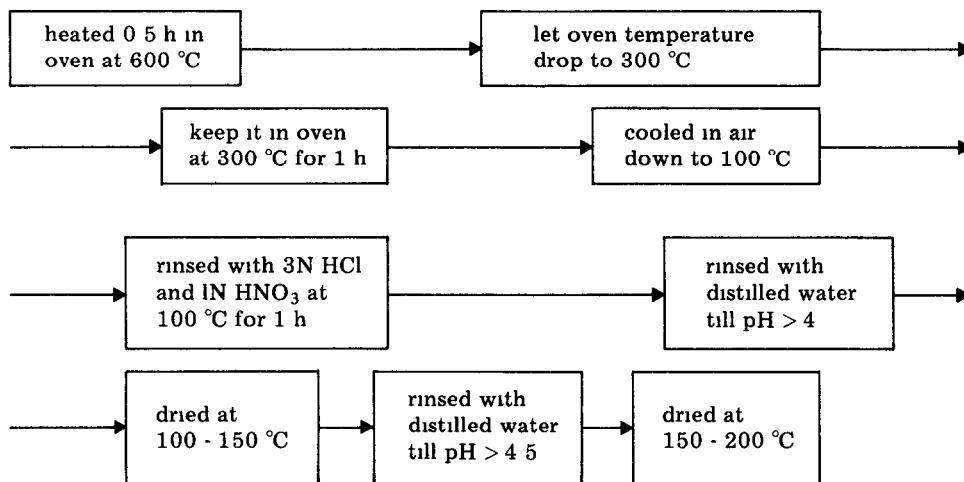


Fig 4 The effect of surface treatments on the graphite electrode in the Ti half cell A<sub>0</sub>, untreated graphite electrode, A<sub>1</sub>, treated graphite electrode, A<sub>2</sub>, Pd impregnated graphite electrode, A<sub>3</sub>, Pd plated graphite electrode, A, platinumized titanium electrode



After this treatment, the anodic polarization could be further reduced by adding Pd to the graphite electrode. There are two ways to add Pd to the electrode, the impregnation method and the plating method.

In the impregnation method, the graphite electrode was first dipped in 10 ml of H<sub>2</sub>O which contained 0.5 g of PdCl<sub>2</sub> and 0.1 g of NaCl, and then dried at 90 °C and 200 °C for 1 h, respectively. After drying, the electrode

was immersed in 2 g/l of  $\text{CH}_3\text{COONa}$  solution for 0.5 h at  $50^\circ\text{C}$ , and 0.02% Pd was reduced on the electrode

In the plating method, the graphite electrode was plated at  $2\text{ mA/cm}^2$  using a solution which contained 3.7 g/l of  $\text{PdCl}_2 \cdot 2\text{H}_2\text{O}$ , 100 g/l of  $\text{Na}_2\text{HPO}_4$ , 20 g/l of  $(\text{NH}_4)_2\text{HPO}_4$  and 2.5 g/l of  $\text{C}_6\text{H}_5\text{COOH}$ . About 0.02% Pd was plated on the graphite electrode

The results for the impregnation method (curve  $A_2$ ) are clearly much better than those for the plating method (curve  $A_3$ ) and are, in fact, comparable with those for the platinized titanium electrode (Engelhard series 3000, platinum thickness  $100\ \mu\text{m}$ ., curve A) which is, however, much more expensive

### 3 Analysis of anodic overpotential

The galvanostatic transient method is widely used in the kinetic study of plating and other electrochemical reactions [11 - 17]. It can analyze the  $IR$  drop in the solution, activation overpotential  $\eta_{\text{act}}$ , and concentration overpotential  $\eta_{\text{conc}}$  directly. This method was applied here to study the anodic overpotential of the electrode during the discharge of the redox battery. Figure 5 shows a typical anodic discharge curve of the inert electrode of a T1 half cell using the galvanostatic transient method. From this curve, one can easily calculate  $IR$ ,  $\eta_{\text{act}}$  and  $\eta_{\text{conc}}$ . Figures 6 and 7 show the relationship between the discharge current density and the activation overpotential and the concentration overpotential, respectively.

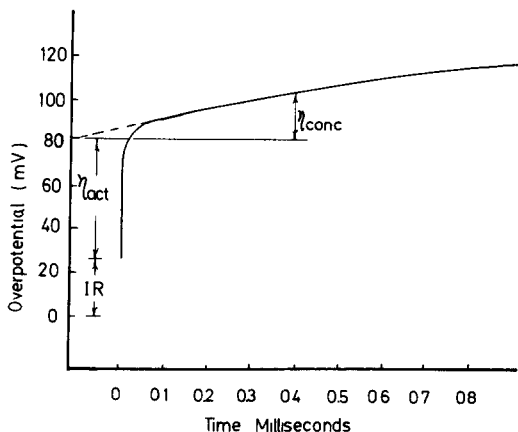


Fig 5 Typical discharge curve of inert electrode of T1 half cell

From Fig 6, the activation overpotential of the T1 half cell (curve  $B_0$ ) was about 30% higher than that of the Fe half cell (curve  $C_0$ ). Figure 7 shows that the concentration overpotential of the T1 half cell (curve  $B_0$ ) was about twice that of the Fe half cell (curve  $C_0$ ).  $B_1$  and  $B_2$  are the results for the impregnation and plating methods, respectively. Both methods result in a reduction of about 40% in the activation overpotential, but whereas the

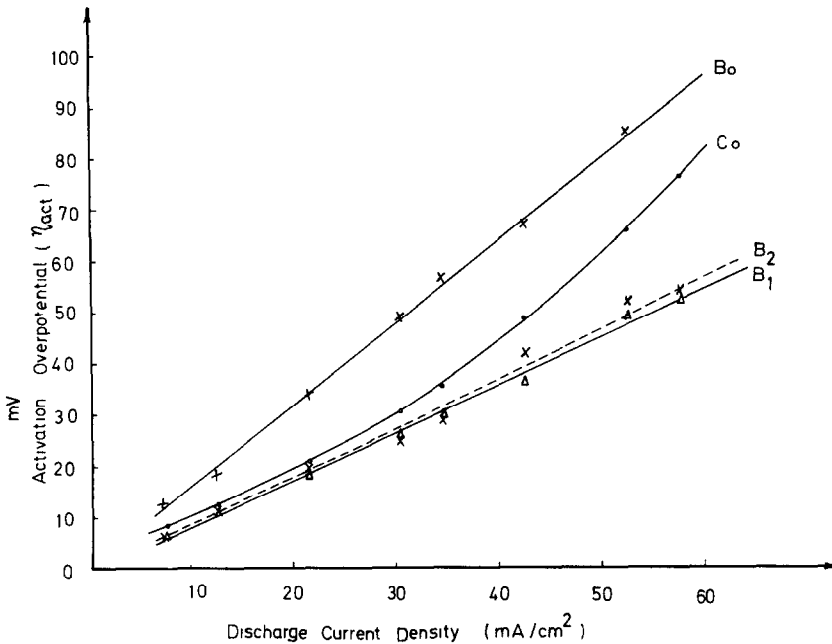


Fig 6 Activation overpotential under galvanostatic transient method for various electrodes B<sub>0</sub>, treated graphite electrode in Ti half cell, C<sub>0</sub>, treated graphite electrode in Fe half cell, B<sub>1</sub>, Pd impregnated graphite electrode in Ti half cell, B<sub>2</sub>, Pd plated graphite electrode in Ti half cell

impregnation method has a large effect on the concentration overpotential, the plating method has a smaller (15 mV less) effect.

It thus appears that at the 0.02% Pd addition level, the graphite still has the predominant influence on the activation overpotential, but the concentration overpotential is sensitive to the method of application of the Pd. It is suggested that deposition of Pd by the impregnation method is instantaneous and results in more nucleation and active sites, thus providing a lower current density and a smaller concentration gradient with a consequent lower concentration overpotential.

From Figs 6 and 7, it can be seen that the major portion of the overpotential in the redox battery during discharge is due to the concentration overpotential. This is quite different from most other electrochemical systems in which there is usually almost no concentration overpotential observed in  $5 \times 10^{-3}$  s [13 - 17].

When the activation overpotential is small (<20 mV), the Butler-Volmer equation reduces to

$$i = i_0 \frac{nF}{RT} \eta_a \quad (1)$$

where  $i$  is the current density,  $i_0$  the exchange current density, and  $\eta_a$  is the anodic overpotential.

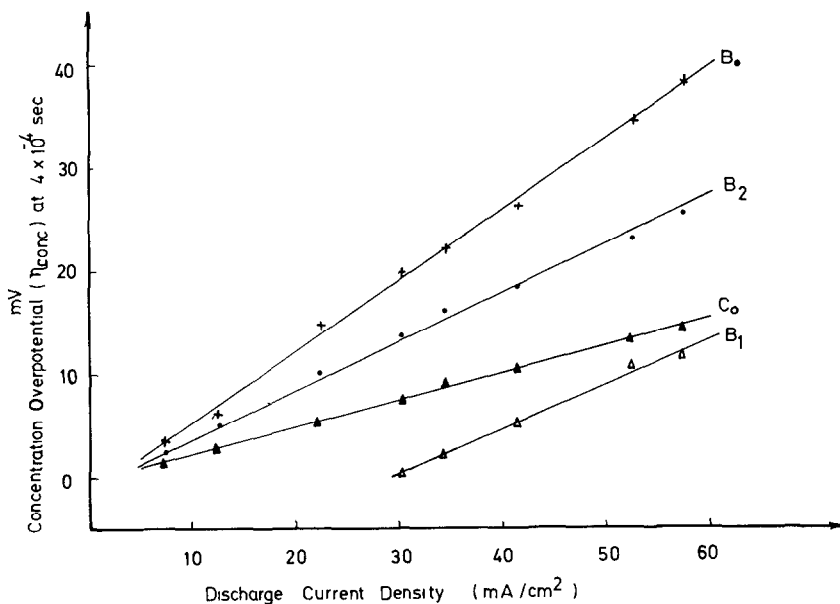


Fig 7 Concentration overpotential under galvanostatic transient method for various electrodes B<sub>0</sub>, treated graphite electrode in Ti half cell, C<sub>0</sub>, treated graphite electrode in Fe half cell, B<sub>1</sub>, Pd impregnated graphite electrode in Ti half cell, B<sub>2</sub>, Pd plated graphite electrode in Ti half cell

TABLE 1

The exchange current density of various electrodes

Electrode	$i_0$ ( $\text{mA}/\text{cm}^2$ )
B <sub>0</sub> Ti half cell	16.1
B <sub>1</sub> Ti half cell, Pd impregnated	27.9
B <sub>2</sub> Ti half cell, Pd plated	27.9
C <sub>0</sub> Fe half cell	25.8

From Fig 6, the exchange current density can be calculated. The results are summarized in Table 1.

#### 4 Optimization of the performance of the Ti/Fe battery

The concentration of the reactants  $[\text{Fe}^{3+}]$ ,  $[\text{Ti}^{3+}]$  and the discharge current density,  $i$ , were considered to be the three major factors that affect the performance of the Ti/Fe redox battery. A statistical approach was adopted to design the experiments necessary for the determination of optimal conditions. Tables 2 and 3 show the experimental data output power,  $Y$ , as a function of  $[\text{Fe}^{3+}]$ ,  $[\text{Ti}^{3+}]$  and  $i$ .



TABLE 2

The experimental conditions for the determination of the battery output power

Factor	Level of coding no						
	-2	$-\alpha$	-1	0	1	$\alpha$	2
[Fe <sup>3+</sup> ] (mole/l)	0 10	0 32	0 80	1 50	2 20	2 68	2 90
[Ti <sup>3+</sup> ] (mole/l)	0 24	0 32	0 48	0 72	0 96	1 12	1 20
$i$ (mA/cm <sup>2</sup> )	2 0	2 9	5 0	8 0	11 0	13 0	14 0

where  $\alpha = 1.68$ 

TABLE 3

The experimental results of the output power of the Ti/Fe battery

Experimental run no	$X_1$	$X_2$	$X_3$	$Y \times 10^6$ (Watt)
1	$\alpha$	0	0	125440
8	$-\alpha$	0	0	164160
7	0	$\alpha$	0	167360
4	0	$-\alpha$	0	108800
9	0	0	$\alpha$	200970
5	0	0	$-\alpha$	73790
2	0	0	0	151040
6	0	0	0	145600
3	0	0	0	149440

 $X_1$  = the coding level of [Fe<sup>3+</sup>] $X_2$  = the coding level of [Ti<sup>3+</sup>] $X_3$  = the coding level of  $i$ 

Performing a second order regression analysis, we have

$$Y = 1480 - 0.118X_1 + 0.143X_2 + 0.315X_3 - 0.0154X_1^2 - 0.0391X_2^2 - 0.0412X_3^2 + 0.0146X_1X_2 - 0.0778X_1X_3 + 0.105X_2X_3 \quad (2)$$

From this equation, it can be found that the maximized output power,  $Y$ , will be located at  $(-\alpha, \alpha, \alpha)$ . Thus, some further experiments (Table 4) were undertaken to confirm this result.

We found that the output power of the Ti/Fe redox battery in our experimental system was maximized when [Fe<sup>3+</sup>] = 0.32M, [Ti<sup>3+</sup>] = 1.12M and  $i = 13$  mA/cm<sup>2</sup>.

## Conclusions

Several conclusions can be reached for the design of a Ti/Fe redox flow battery

TABLE 4

Supplemental experiments for the determination of optimal conditions

Experimental run no	$X_1$	$X_2$	$X_3$	$Y \times 10^6$ (Watt)
4	$-\alpha$	$\alpha$	$\alpha$	223600
5	$-\alpha$	$\alpha$	$\alpha$	215800
1	$-\alpha$	$\alpha$	$\alpha$	221000
2	-2	2	2	176400
3	-2	2	2	168000
6	-2	2	2	170240

(1) Increasing the surface area of the inert electrode, and the use of the impregnation method to add Pd to the graphite electrode in the Ti half cell, can reduce electrode overpotential significantly

(2) A high reactant flow rate in the Ti half cell is essential, as the concentration polarization of the Ti half cell is the limiting factor

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