

A method for evaluating the performance of positive electrode grids of lead/acid batteries

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Received 18 November 1996; accepted 27 January 1997

Abstract

For a battery plate to function satisfactorily, there must be a good contact at the interface between the grid and active material. This is because the adhesion of the active material strongly effects the cell performance. The adhesion of the active material changes due to the state of the interface between the grid and active material. In this study, the adhesion of active material is examined by evaluation of the grid surface. A grid with good adhesion of the active material has the following characteristics: (i) the change in the rest potential is fast; (ii) the lead sulfate membrane formed on the grid surface is thin, and (iii) the change in potential during the oxidation is slow. Good or bad adhesion of the active material can be judged using an evaluation method based on these criteria. The annealing treatment of the grid is investigated using this evaluation method. The optimum conditions of annealing are 170 °C and 24 h. © 1997 Elsevier Science S.A.

Keywords: Lead/acid batteries; Positive electrode grids; Adhesion; Active materials

1. Introduction

Lead/acid batteries are irreversibly damaged not only by excessive overdischarge, but also by prolonged storage in a fully-discharged state. The positive electrode exerts a strong effect on battery performance. The positive grid is irreversibly degraded by a series of corrosion reactions. This early failure is attributed to the development of an insulating barrier layer at the interface between the positive grid and the active material [1]. Many researchers have studied the mechanism of the anodic corrosion of lead in sulfuric acid [2–7]. Pregarman [8] has reported that the microstructure as well as the composition of Pb–Ca–Sn alloys influence their corrosion behaviour. The structure of the interface between the grid and the active material plays an important role in the irreversible deterioration of batteries. The surface state and the electrochemical behaviour of the grid are also important [9]. For example, the adhesion of active material is significantly influenced by the state of the interface between the grid and active material. Degradation of the adhesion results in a decrease in cell performance [10].

The purpose of this paper is to develop a method for evaluating positive electrode grids. Using this evaluation method, improvements in the grid surface have been examined.

2. Experimental

A Pb–0.08wt.%Ca–2.20wt.%Sn alloy was used for the grid of the positive electrode. The grids were annealed in air between 25 and 320 °C for 72 h. The rest potential of the grid sulfuric acid solution was determined. The grid was galvanostatically oxidized anodically in 6.3 M H₂SO₄ at 0.1 mA cm⁻² after the rest potential was measured. The potential was measured during the oxidation. All potential values are reported versus a Hg/Hg₂SO₄ reference electrode. A platinum plate was used as the counter electrode. All experiments were performed at 25 °C.

After immersion for two days, the grid was washed with distilled water and acetone, and then dried. The surface and cross section of the grid were examined by scanning electron microscope (SEM) (JOEL JSM-T330A) and by X-ray diffraction (XRD) (RIGAKU RAD-C).

3. Results and discussion

The adhesion of active material is one of the important factors controlling cell performance. The surface state of the positive grid significantly affects the adhesion of active material. Thus, it is very important to evaluate the surface state of the grid. A good grid means that only small amounts of active material become detached.

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Table 1
Condition of the grids

Sample	Adhesion of active material	Cooling speed of casting
A	Good	Cool down to room temperature
B	Bad	Cool down to room temperature
C	Bad	Quench in water

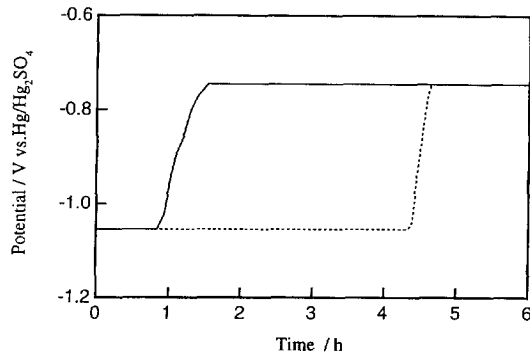


Fig. 1. Rest potential vs. time for various grids in 6.3 M H_2SO_4 . (—) sample A, and (---) sample B.

3.1. Evaluation method for the positive electrode grid

3.1.1. Lead sulfate formed on the surface of grid

The condition of the grids is shown in Table 1 and Fig. 1. The change in rest potential with time is different for grids with different adhesion of the active material. For example, the change in rest potential of the grid (sample A) with good adhesion is faster than those (e.g. sample B) with poor adhesion.

The XRD patterns of the electrode, which were obtained both before and after the change in rest potential are shown in Fig. 2. Lead sulfate peaks are detected after the change in potential. It is concluded that a membrane of lead sulfate is formed on the surface of grid. The time during which the rest potential changes is called the 'sulfation time'. This parameter reflects the oxidation state of the grid.

Differences in the sulfation time are caused by differences in the cooling speeds after casting. This is because the latter strongly affect the surface condition of the grid. The sulfation time of sample C is very long (Table 2). Such a grid requires a large quantity of lead sulfate to fully cover on the entire surface. When a large amount of lead sulfate exists at the interface between the grid and the active material, it is highly probable that cracks will form between the grid and the active material. As a result, the adhesion is expected to decrease. Thus, it is concluded that adhesion of the active material decreases with increase in sulfation time.

3.1.2. The formation process of lead sulfate

Figs. 3 and 4 show SEM photographs of the surface and a cross section of the grids after immersion in sulfuric acid solution for 2 days. It can be seen that many lead sulfate

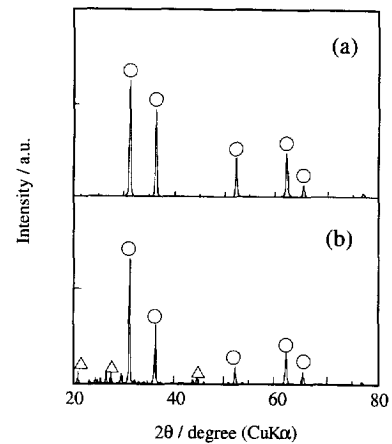


Fig. 2. XRD patterns of the grid (a) before and (b) after rest potential change: (○) Pb, and (△) $PbSO_4$.

Table 2
Sulfation time of various grids

	Sulfation time (h)
sample A	1.3
sample B	4.3
sample C	19.5

particles are formed on the surface of the grid after the change in rest potential, with the various grids. Different sizes and shapes of particle are observed, as well as different thicknesses of membrane. Large lead sulfate particles form a thin membrane on the grid with good adhesion (sample A). Small lead sulfate particles form a thick membrane on the grid with bad adhesion (sample B). Small lead sulfate particles produce a very thick membrane on the grid (sample C) that was quenched.

The density of lead sulfate produced as the discharge product of lead is smaller than that of active material (lead dioxide) of the positive electrode. In other words, the volume of lead sulfate is larger than that of lead dioxide. Thus, it is considered that a stress is imposed by the increase in volume of the product at the interface between the grid and the active material. Consequently, the adhesion of the active material decreases when large amounts of lead sulfate form a thick membrane on the grids (e.g. samples B and C).

3.1.3. Oxidation process of the grid

When the grid was galvanostatically oxidized with an anode current of 0.1 mA cm^{-2} , the potential of each grid increased from -1.0 to 1.6 V (see Fig. 5). The time during which the potential changes is called the 'oxidation retention time'. In the case of a grid with bad adhesion (samples B and C), the change in oxidation retention time is comparatively fast.

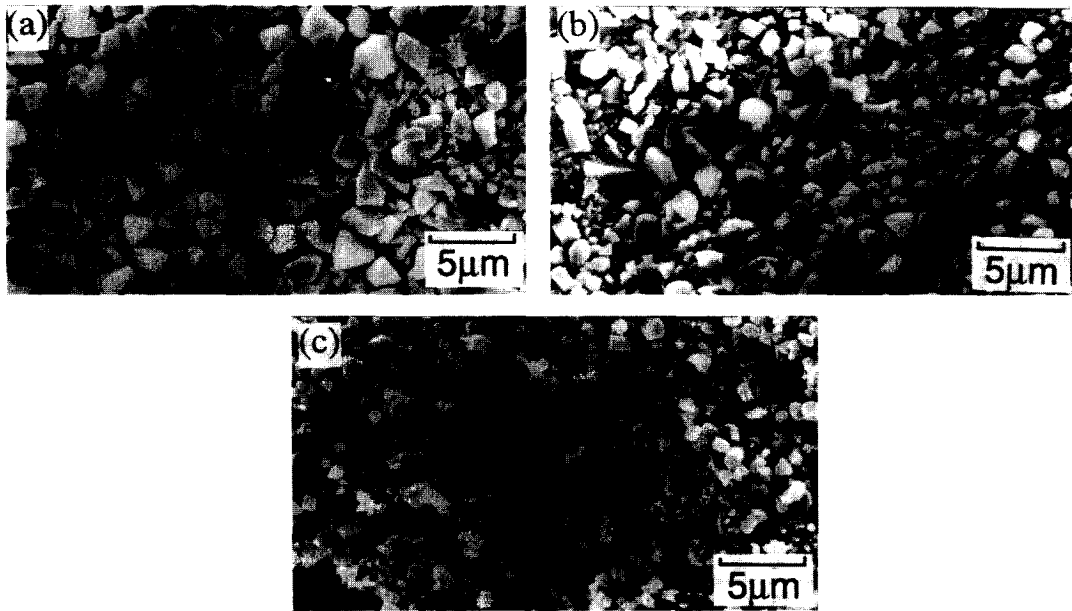


Fig. 3. SEM graphs of the surface of the grids after immersion in 6.3 M H_2SO_4 : (a) sample A; (b) sample B, and (c) sample C. Grids were immersed into 6.3 M H_2SO_4 for 2 days, and washed it with distilled water and acetone, then dried.

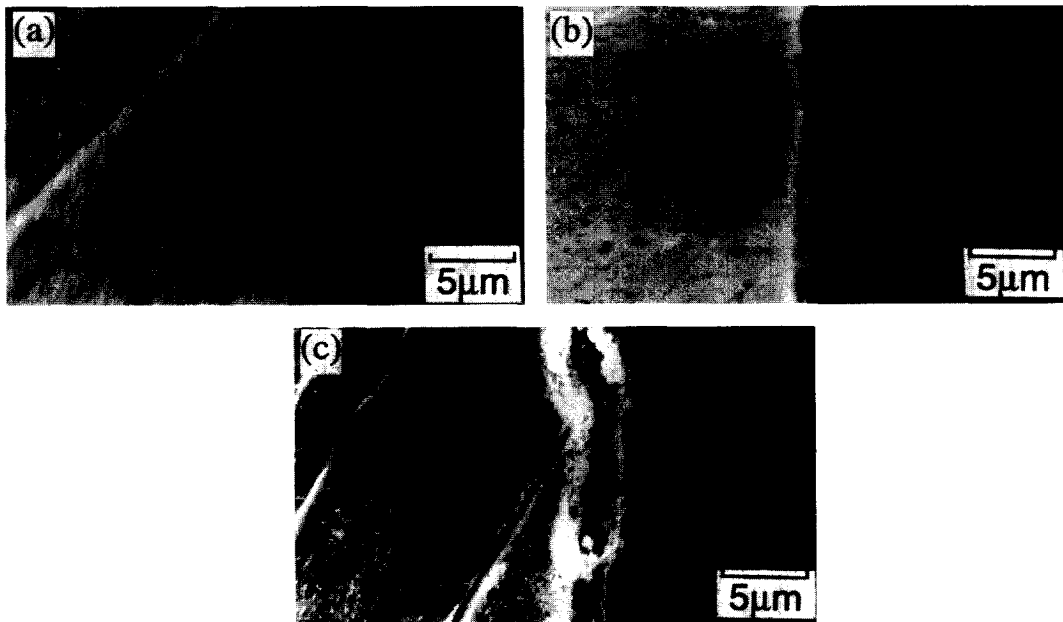


Fig. 4. SEM photographs of the cross sections of the grids after immersion in 6.3 M H_2SO_4 : (a) sample A; (b) sample B, and (c) sample C. Grids were immersed into 6.3 M H_2SO_4 for 2 days, and washed it with distilled water and acetone, then dried.

The XRD patterns of an electrode before and after the potential change are shown in Fig. 6. Peaks for lead dioxide and lead sulfate appear with change in the potential. Thus, a membrane of lead sulfate and lead dioxide is formed on the surface of the grid.

For grids with a short oxidation retention time, it is easy to corrode the grid and form a corrosion layer between the grid and active material. When a thick corrosion layer is produced on the surface of the grid, it is easy to form a crack between the grid and active material. As a result, the adhesion

of the active material decreases. Therefore, the adhesion of active material decreases when the oxidation retention time is short.

In summary, good or bad adhesion of the active material can be determined by the evaluation method described in Table 3.

3.2. Modification of grid surface

The interface structure between the grid and active material, as well as the surface state and the electrochemical behav-

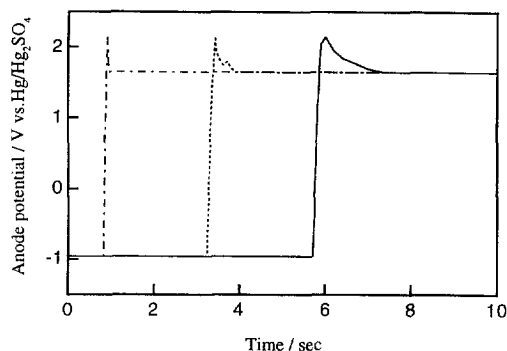


Fig. 5. Anode potential curves for various grids in 6.3 M H_2SO_4 at a current density of 0.1 mA cm^{-2} : (—) sample A; (· · ·) sample B, and (- · -) sample C.

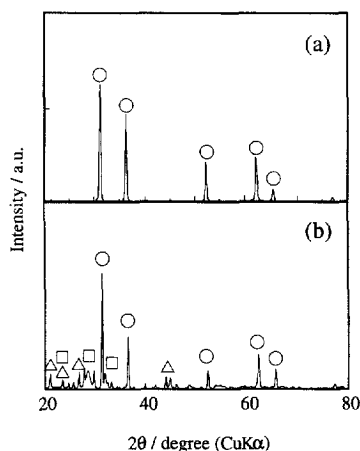


Fig. 6. XRD patterns of the grid (a) before and (b) after potential change: (○) Pb; (△) PbSO_4 , and (□) PbO_2 .

ior of the grid itself play an important role in the adhesion of the active material. The effect of annealing treatment, which is an after-treatment of the grid, has been investigated using the above-mentioned evaluation method.

3.2.1. Annealing temperature

The colour of the grid surface changes to a light yellow during annealing at a temperature of $\sim 170^\circ\text{C}$, and turns black via grey with increasing annealing temperature. Although, the XRD is formed on the grid surface. It is considered that the oxidation states of the grid surface varied with changing annealing temperature. Fig. 7 shows the change in both sulfation time and oxidation retention time at

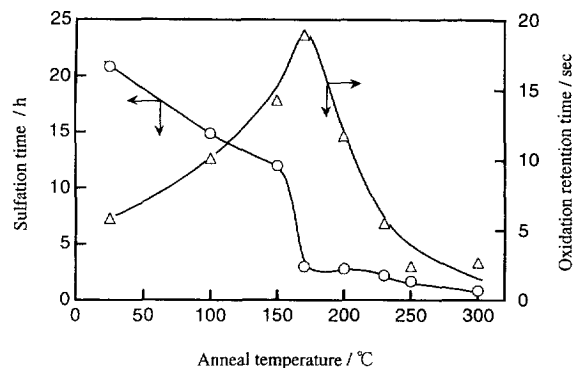


Fig. 7. Effect of the annealing temperature on (○) sulfation time and (△) oxidation retention time. Grids annealed in air for 24 h at various temperatures; electrolyte: 6.3 M H_2SO_4 , and oxidation current density: 0.1 mA cm^{-2} .

different annealing temperatures. The sulfation time decreases with increasing temperature; it decreased rapidly at 170°C , then remained almost constant at temperatures over 170°C . The oxidation retention time increases with increasing temperature and to reach a maximum at 170°C . Fig. 8 shows SEM photographs of the grid surface annealed at various temperatures. The largest size of the lead sulfate formed on the grid surface is obtained at 170°C . The differences in oxidation state of the grid exert a great effect on the formation of lead sulfate on the grid surface. As a result, it is found that the optimum temperature of annealing is 170°C .

3.2.2. Annealing time

The colour of the grid surface changes to grey with increasing annealing time although the XRD patterns are almost the same. It is considered that the oxidation states of the grid surface vary with change in annealing time. Fig. 9 shows the change in sulfation time and oxidation retention time for various annealing times. The sulfation time decreases rapidly with increasing annealing time, and it stays almost constant after 24 h. The oxidation retention time increases rapidly with increasing annealing time and it remains almost constant after about 12 h.

From the above results, it is concluded that the best annealing time is 24 h. Fig. 10 shows SEM photographs of the grid surface annealed for various times. The lead sulfate crystals formed on the grid surface is large for each annealing times at 170°C . The largest particles of lead sulfate are formed on the grid at 24 h. The differences in the oxidation state of the grid exert a significant effect on the formation of lead sulfate

Table 3
Methods for grid evaluation

	Grid with good adhesion of active material	Grid with bad adhesion of active material
Sulfation time	Short	Long
Oxidation retention time	Long	Short
Formation particle	Large	Small

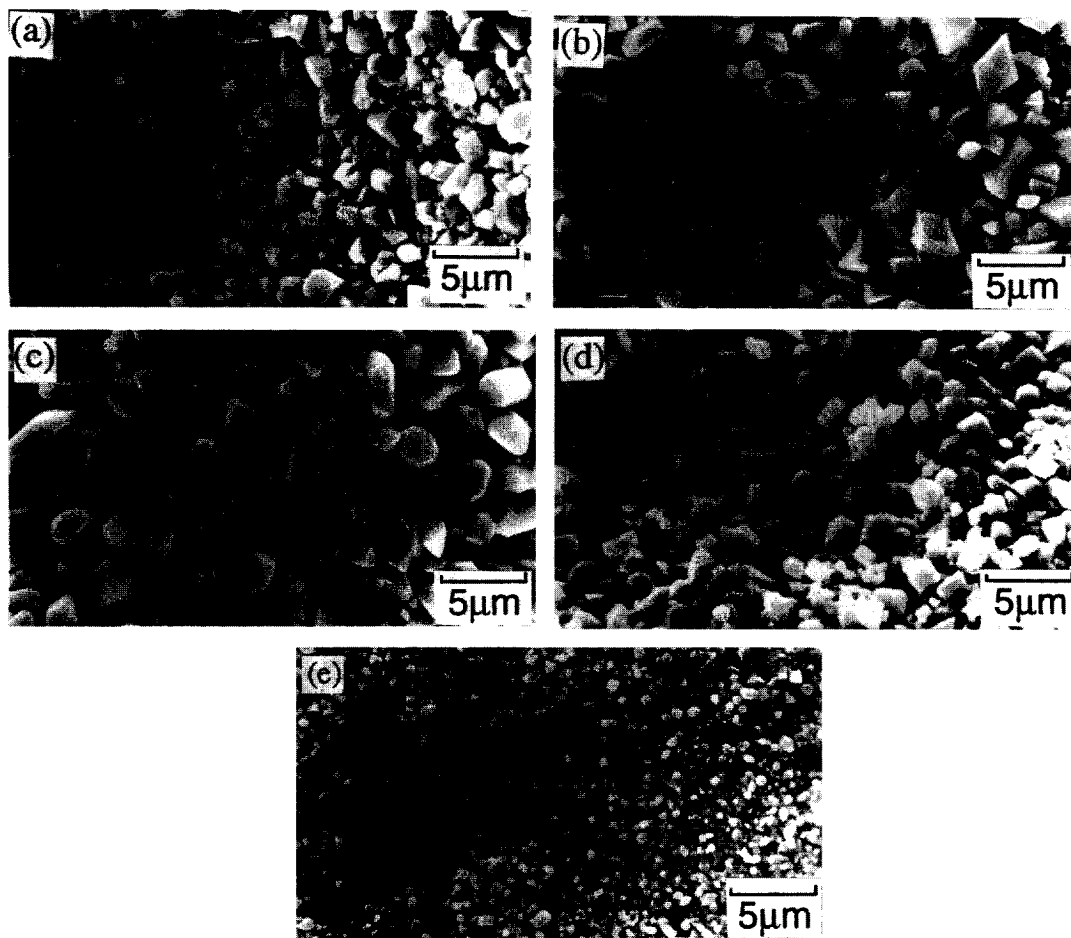


Fig. 8. SEM photographs of the grid surface at various annealing temperatures: (a) room temperature; (b) 100 °C; (c) 170 °C; (d) 200 °C, and (e) 250 °C.

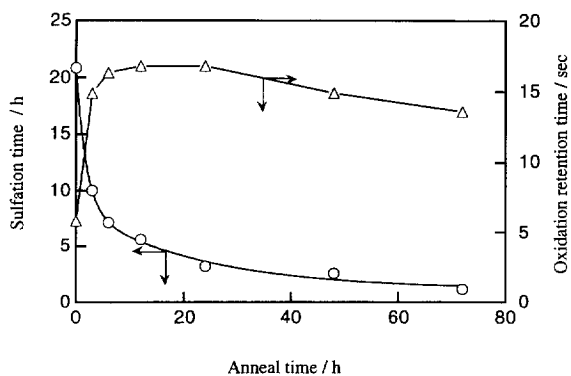


Fig. 9. Effect of the annealing time on (○) sulfation time and (△) oxidation retention time. Grids annealed in air at 170 °C for various anneal times. Electrolyte: 6.3 M H₂SO₄; oxidation current density: 0.1 mA cm⁻².

on the grid surface, i.e. the influence is the same as that of the annealing temperature.

In summary, it is found that the surface state is strongly affected by the early stage of the annealing treatment. The

best condition for annealing is 170 °C for 24 h. It is thought that the annealing treatment improves the adhesion of the active material since large and thin crystals of lead sulfate are formed on the surface of the grid.

4. Conclusions

The surface condition of grid strongly affects the adhesion of the active material. An evaluation method has been investigated using grids with different active material. The adhesion of active material is estimated by analysis of the grid surface.

This evaluation method is composed of three measurements: (i) sulfation time; (ii) SEM observations of lead sulfate particles formed on the grid surface, and (iii) the oxidation retention time.

A good grid has the following conditions: (i) the sulfation time is long; (ii) the lead sulfate particles are large, and (iii) the oxidation retention time is long.

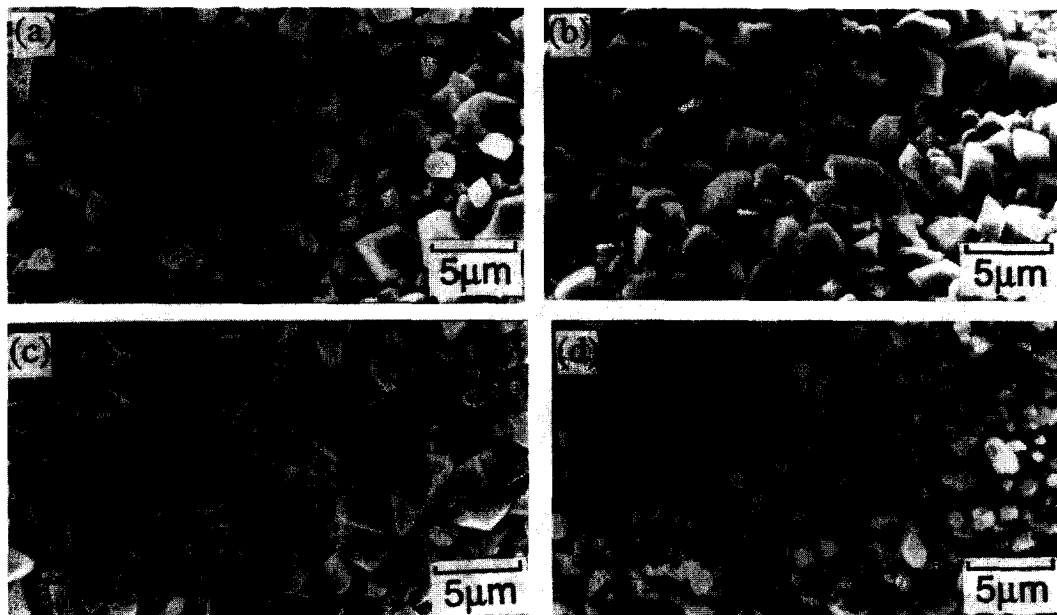


Fig. 10. SEM photographs of the grid surface at various annealing times: (a) 3 h; (b) 6 h; (c) 24 h, and (d) 72 h.

Studies show that the surface state of the grid is strongly influenced by the early stage of the annealing treatment. The optimum treatment is 170 °C and 24 h.

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