Oxygen Evolution Reaction on Composite Cobalt Borides

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The Oxygen evolution reaction on cobalt borides and composite cobalt borides was investigated in a 6 M KOH solution (1 M = 1 mol dm^{-3}) using the factor of the magnetic properties. In the system of cobalt borides (Co:B = 3:1) prepared at various sintering temperatures, the boride having a higher saturation magnetization revealed a higher activity of the oxygen evolution reaction. In the system of composite cobalt borides which have various magnetic moments, μ_B, a clear correlation between the activity of the oxygen evolution reaction and the saturation magnetization (or magnetic moment, μ_B) was observed for several composite cobalt boride species (*i.e.*, Co-Fe-B, Co-Ni-B, Co-Mn-B, and Co-B). Among the composite cobalt boride species, the cobalt iron boride (Co:Fe:B = 1:2:1) sintered at 450 °C showed the highest activity of oxygen evolution reaction in a 6 M KOH solution. The conditions of oxide formation on Co-Fe-B(1:2:1) and on Co-B(3:1) in a 6 M KOH solution were compared with those on cobalt by means of voltammetry and chronopotentiometry. It was concluded that the ease and stability of oxide films in higher oxidation states are strongly correlated to the activity of the oxygen evolution reaction which occurs on more highly oxidized oxide films.

Oxygen evolution reaction on non-noble metals or alloys is attractive in the field of oxygen electrode catalysts because of the demand for low-cost electrocatalyst materials for water electrolyzers. The transition metal borides have been reported to have a high activity for an oxygen evolution reaction in an alkaline solution.[1] In the present paper, we will focus on the cobalt boride and investigate the activity of the oxygen evolution reaction on composite cobalt borides in terms of the factor of magnetic properties.

Experimental

The composite cobalt borides were prepared by mixing the powders of cobalt, the other transition metal (Fe, Ni, or Mn), and amorphous boron in a proper atomic ratio. The mixed powders, whose particle sizes were adjusted by means of 200 mesh sieve, were pressed with 10 t cm^{-2} into a cylinder shape (0.7 cm in diameter). The cylindrical samples were sintered for 4 h in an Ar gas atmosphere at several temperatures. The identification and characterization of the composite cobalt borides were performed by means of an X-ray diffractometer, a differential thermal analyzer, an X-ray photoelectron spectroscopy, and a magnetic-property analyzer (sensitive vibrating sample magnetometer). The surface conditions and roughness of the electrodes were examined by means of a scanning electron microscope and a stylus technique (Talystep). The mean surface roughness[†] of the boride electrodes became lower with the increase in the sintering temperature, reaching a constant value of 0.6 μm at a sintering temperature of more than 400 °C. The SEM observation showed that the surface of borides sintered at more than 300 °C for 4 h is non-porous.[††] The current *vs.* potential curves with IR correction for oxygen evolution reaction on the composite cobalt borides were measured potentiostatically in a 6 M KOH solution at 25 °C under an N_2 atmosphere. After having been covered by epoxy resin, the working electrode was carefully polished with emery paper, and then it was washed with ethanol and water. The boride electrode was used after pretreatment consisting of anodic oxidation for 1 h at 0.80 V (Hg-HgO) in the case of the oxygen evolution reaction in order to obtain stable oxidized surface condition. The activation energy of the oxygen evolution reaction was evaluated by means of the apparent activation energy at 0.60 V (Hg-HgO) (or at proper potential) and it was determined in the temperature range between 0 °C and 50 °C with the temperature correction. The electrochemical investigation of electrode surface oxides was done in a 6 M KOH solution by means of linear potential sweep voltammetry and chronopotentiometry. A mercury-mercury(II) oxide electrode in the same solution was used as the reference electrode, and all the potential was referred to the Hg-HgO electrode. The stability of the borides was evaluated by means of the amount of boron dissolved after 24 h electrolysis at 0.70 V in the 6 M KOH solution. The amount of boron dissolved in the solution was examined by means of photospectroscopy using the Methylene Blue method. A small amount of boron dissolved was detected as having values between 2 and 4 mg after 24 h electrolysis for the three cases of Co-B(3 : 1), Fe-B(3 : 1), and Co-Fe-B(1 : 2 : 1), which were sintered at 400 or 450 °C.

Results and Discussion

Oxygen Evolution Reaction on Cobalt Borides. It was found that the cobalt boride at proper conditions has a higher activity for oxygen evolution reaction than does nickel or cobalt in an alkaline solution.[1] The activity of the oxygen evolution reaction depends

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[†] The mean surface roughness is evaluated by averaging 10 point data of ΛR_{max} (difference between top and bottom positions as measured by Talystep).

[††] The double layer capacities of Co, Co-B(3 : 1) sintered at 400 °C, and Co-Fe-B(1 : 2 : 1) sintered at 450 °C, measured at −1.0 V and at 1 kHz in 6 M KOH, were observed as the reasonable values of 110, 60, and 110 μF cm^{-2} respectively. The current-potential curve on the Co electrode, which was prepared by the same method as the borides, was observed to show the same behavior as on an usual Co electrode. These two facts also strongly support the theory that these borides can be used as non-porous states.

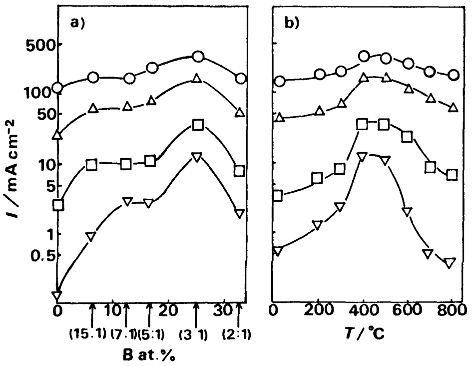

Fig. 1. Effects of sintering temperature and boron content of cobalt borides on oxygen evolution current in 6 M KOH at 25 °C.
a) Oxygen evolution current *vs.* boron content curves on Co–B sintered at 400 °C for 4 h. b) Oxygen evolution current *vs.* sintering temperature curves on Co–B(3 : 1), ○: at 0.80 V, △: at 0.70 V, □: at 0.60 V, ▽: at 0.50 V.

largely on the composition ratio of Co:B and the sintering temperature. The effects of the boron content and the sintering temperature on the activity of the oxygen evolution reaction (*i.e.*, current values at several constant potentials) are demonstrated in Fig. 1. The best conditions for a high activity of oxygen evolution were obviously observed to be at the composition ratio of Co:B=3:1 and at the sintering temperature=400—500 °C, as may be seen in Fig. 1. The apparent activation energy, ΔH, at 0.60 V, of the oxygen evolution reaction on cobalt boride sintered at 400—500 °C, gave the lowest value of 8.6 kcal mol^{-1}.[†††] As has already been pointed out in Ref. 1, the cobalt boride sintered at 400 °C is considered to be amorphous or in a transition state, judging from the combined results of X-ray diffraction analysis, differential thermal analysis, and magnetic property measurement. The magnetic properties which are sensitive to the structure change in materials were measured and discussed in Ref. 1 in connection with the function of the sintering temperature. A rapid decrease in coercivity, *Hc*, was observed in the range of sintering temperature between 350 and 400 °C. The saturation magnetization, σ_s, also started to change from the sintering temperature of 300 °C and showed its maximum in the sintering temperature region between 350 and 500 °C. In the region of sintering temperatures, higher than 500 °C, the value of σ_s abruptly decreased. The change in magnetic properties from the lower sintering temperature, at which the peaks of X-ray diffraction analysis and DTA caused by the formation of compounds are not recognized (*cf.* Ref. 1), may indicate that the amorphous or transition state compounds are formed in the range between 400 and 500 °C.[**]

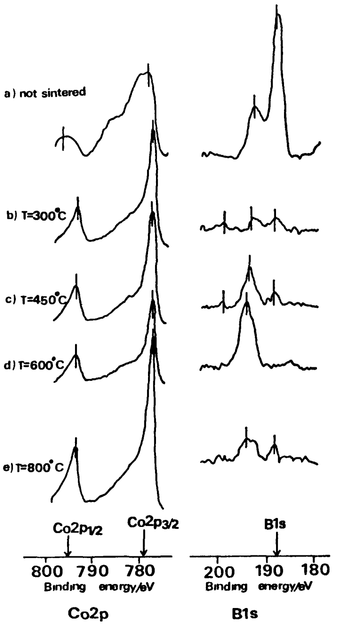

Fig. 2. Photoelectron spectra of Co 2p levels and B 1s level for Co–B(3 : 1) at various sintering temperatures.

Since X-ray photoelectron spectroscopy (XPS) is a powerful technique for the investigation of bonding in transition metal compounds, the XPS measurements were performed in order to confirm the formation of compounds. The XPS spectra of the Co 2p and B 1s levels are shown in Fig. 2 as a function of the sintering temperature. The spectra were measured after pretreatment of 5 min Ar^+ sputtering. The peak values of the metal states, which are given by arrows in the figure, have been reported to be 794.0 and 779.0 eV for Co $2p_{1/2}$ and $2p_{3/2}$ respectively and 188.1 eV for the B 1s state.[2,3] The chemical shifts for the Co $2p_{3/2}$ and $2p_{1/2}$ were observed to become the lower energy level at a sintering temperature of more than 300 °C. The chemical shifts for the Co $2p_{3/2}$ level reach a constant value of 1.0 eV from the sintering temperature of 300 °C. In the case of the Co $2p_{1/2}$ level, the shifts give 0.7 eV at 300 °C and close to the final value of 1.0 eV at 800 °C with the increase in the sintering temperature. In the spectra of the B 1s level, there appear two peaks, at 188.9 eV and in the range between 193 and 194 eV. In the range of sintering temperatures between 300 and 450 °C, where the oxygen evolution reaction on cobalt borides shows the highest activity, the spectra show unclearly three small peaks (the peak at 199.5 eV was newly observed), which might be satellite peaks caused by the exchange splitting of the B 1s level with the unpaired valence electrons under amorphous conditions. It can be also confirmed from the above results, shown in Fig. 2, that the compounds of cobalt borides showing amorphous or transition state conditions are formed in the range of sintering temperatures between 300 °C and 500 °C.

The magnetic properties of 3d transition-metal alloys are strongly connected to the electron numbers of 3d

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[†††] 1 kcal mol^{-1}=4.184 J mol^{-1}.

[**] The X-ray diffraction peak of CoB was partially observed at 400 °C, while the peaks of Co_3B were detected from 600 °C.

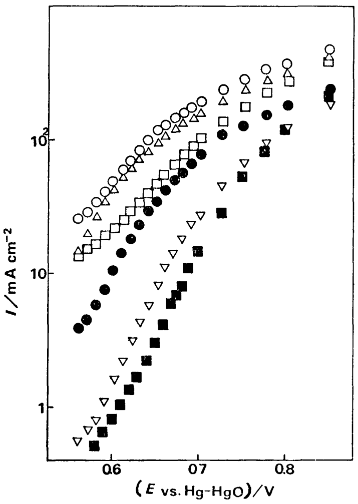

Fig. 3. Oxygen evolution current *vs.* potential curves on various composite cobalt borides in 6 M KOH at 25 °C.
○: Co-Fe-B(1 : 2 : 1) sintered at 450 °C, ●: Co-Ni-B(3 : 3 : 2) sintered at 400 °C, □: Co-B(3 : 1) sintered at 400 °C, △: Co-Fe-B(3:3:2) sintered at 450 °C, ▽: Co-Mn-B(3 : 3 : 2) sintered at 400 °C, ■: Co.

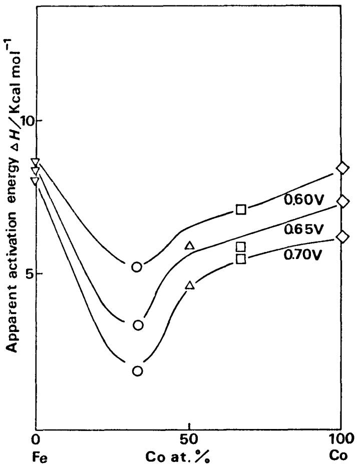

Fig. 4. Effect of cobalt or iron content of Co-Fe-B (Metal : B = 3 : 1) on apparent activation energy at various potentials (0.60, 0.65, and 0.70 V) in 6 M KOH.
○: Co-Fe-B(1 : 2 : 1) sintered at 450 °C, △: Co-Fe-B(3 : 3 : 2) sintered at 450 °C, □: Co-Fe-B(2 : 1 : 1) sintered at 450 °C, ◇: Co-B(3 : 1) sintered at 450 °C, ▽: Fe-B(3 : 1) sintered at 400 °C.

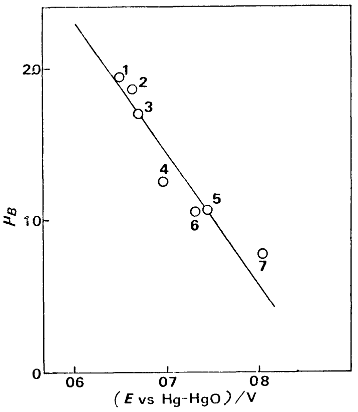

Fig. 5. Relationship between magnetic moment and activity of oxygen evolution reaction (expressed as potential at 0.1 A cm^{-2}) on composite cobalt borides in 6 M KOH at 25 °C.
1: Co-Fe-B(1 : 2 : 1) sintered at 450 °C, 2: Co-Fe-B(3 : 3 : 2) sintered at 450 °C, 3: Co-B(3 : 1) sintered at 400 °C, 4: Co-B(3 : 1) sintered at 600 °C, 5: Co-B (3 : 1) sintered at 800 °C, 6: Co-Ni-B(3 : 3 : 2) sintered at 400 °C, 7: Co-Mn-B(3 : 3 : 2) sintered at 400 °C.

plus 4s, and they are usually discussed with the magnetic moment, μ_B, expressed by Bohr magnetons. The magnetic moment, μ_B, can be calculated from σ_s by using the following equation:

$$\mu_B = M/\beta = A\cdot\sigma_s/(N\cdot\beta), \qquad (1)$$

where M, A, N, and β are magnetic moment per atom, the atomic mass, the Avogadro constant, and the unit of the Bohr magneton respectively. Since the saturation magnetization of cobalt borides reaches a maximum in the range where the activity of oxygen evolution reaction becomes the highest, the saturation magnetization, σ_s, or the magnetic moment, μ_B, may be one of the most important factors which are correlated to the activity. Therefore, we tried to form the composite cobalt borides by referring to the Slater-Pauling curves,[5] which demonstrate the relationship between μ_B and the electron number of the outer-most orbitals (3d+4s) in the case of 3d transition-metal alloys. In the Slater-Pauling curves, the 30% Co–Fe alloy has the maximum value of μ_B=2.5.

Oxygen Evolution Reaction on Composite Cobalt Borides. The current *vs.* potential curves for oxygen evolution reactions with IR correction on several composite cobalt borides and cobalt in a 6 M KOH solution are demonstrated in Fig. 3. Among the composite cobalt borides, the cobalt boride containing iron (Co–Fe–B), which has a higher saturation magnetization value than that of the cobalt boride species, gives the highest activity of oxygen evolution reaction, as may be seen in Fig. 3. The activity order of composite cobalt borides is as follows:

$$\text{Co-Fe-B}(1:2:1) > \text{Co-Fe-B}(3:3:2) > \text{Co-B}(3:1) >$$
$$\text{Co-Ni-B}(3:3:2) > \text{Co-Mn-B}(3:3:2) > \text{Co},$$

where the almost composite cobalt borides were sintered at 400 or 450 °C for 4 h. The effect of the iron composition ratio of composite cobalt borides (Co–Fe–B) was evaluated by means of the apparent activation energy at 0.60, 0.65, and 0.70 V as is shown in Fig. 4, where the sintering temperature was fixed at 450 °C, at which temperature the Co–Fe–B species usually gives the highest activity of the oxygen evolution reaction. In Fig. 4, the cobalt iron boride with Co:Fe:B=1:2:1 shows the lowest apparent activation energy, namely, the highest activity of the oxygen evolution reaction (*e.g.*, ΔH at 0.60 V=5.2 kcal mol^{-1}). The results correspond well to the information from the Slater-Pauling curves, where the 30% Co–Fe alloy has the maximum μ_B value of 2.5.

The relationship between the activity of the oxygen evolution reaction and the magnetic moment, μ_B, is demonstrated in Fig. 5, where the activity is expressed as the potential at a constant oxygen evolution current, 0.10 A cm^{-2}. As has previously been supposed, the above relation has a clear linear correlation, the composite cobalt boride with the higher μ_B gives the higher activity of the oxygen evoulution reaction. Since the magnetic moment, μ_B, is correlated to the numbers of unpaired electrons in the 3d transition metal alloys, the number of unpaired electrons is considered to be the most important factor in determining the activity of the oxygen evolution reaction in the composite cobalt boride species. The oxygen evolution reaction, however, occurs not on bare boride, but on oxidized boride. Therefore, the magnetic moment or the number of unpaired electrons may be connected with the ease of surface oxide film formation, which frequently affects the oxygen evolution reaction because the oxygen evolution reaction occurs in many cases on oxide films. Since the formation and conditions of oxide films can be strongly correlated to the activity of the oxygen evolution reaction on composite cobalt borides, the conditions of oxide films on Co–Fe–B and on Co–B with the higher activity will, in the next section, be investigated by means of linear potential sweep voltammetry and chronopotentiometry by comparing the oxide conditions of cobalt in a 6 M KOH solution.

Electrochemical Investigation of Surface Oxide on Cobalt, Cobalt Boride, and Cobalt Iron Boride in a 6 M KOH Solution. A Typical linear potential sweep voltammogram and a chronopotentiogram on cobalt in a 6 M KOH solution are shown in Fig. 6. The behavior of the linear potential sweep voltammogram is almost the same as that in 0.2—8 M KOH solutions reported by Behl and Toni.[6] They discussed the five peaks and concluded that the following reaction scheme holds for the electrooxidation of cobalt in a KOH solution:

$$\mathrm{Co} + 2\mathrm{OH}^- \rightarrow \mathrm{Co(OH)_2} + 2e \qquad \text{Peak 1 and 2} \tag{2}$$

$$\mathrm{Co} + 2\mathrm{OH}^- \rightarrow \mathrm{CoO} + \mathrm{H_2O} + 2e \qquad \text{Peak 2} \tag{3}$$

$$3\mathrm{Co(OH)_2} + 2\mathrm{OH}^- \rightarrow \mathrm{Co_3O_4} + 4\mathrm{H_2O} + 2e \qquad \text{Peak 3} \tag{4}$$

$$\mathrm{Co(OH)_2} + \mathrm{OH}^- \rightarrow \mathrm{CoOOH} + \mathrm{H_2O} + e \qquad \text{Peak 4} \tag{5}$$

$$\mathrm{CoOOH} + \mathrm{OH}^- \rightarrow \mathrm{CoO_2} + \mathrm{H_2O} + e \qquad \text{Peak 5 .} \tag{6}$$

In Fig. 6, the Peak 3 is not clear in the voltammogram, but it is detectable at an enlarged scale. It is likely that the first film formed on cobalt is cobalt(II) hydroxide and that the cobalt(II) oxide films are formed after hydroxide formation. Finally, the more highly oxidized oxide films, such as $\mathrm{Co_3O_4}$, CoOOH, and $\mathrm{CoO_2}$, begin to form at the more anodic oxidation. The same conclusion can be drawn from our results for linear potential sweep voltammogram judging from the similar behavior in Fig. 6(a). The behavior of the chronopotentiogram shown in Fig. 6(b) is similar to that of the linear potential sweep voltammogram, but only three waves are observed. The first large wave corresponds to the hydroxide film formation, while the small second and third waves are connected with the more highly oxidized oxide film formation.

The linear potential sweep voltammograms and

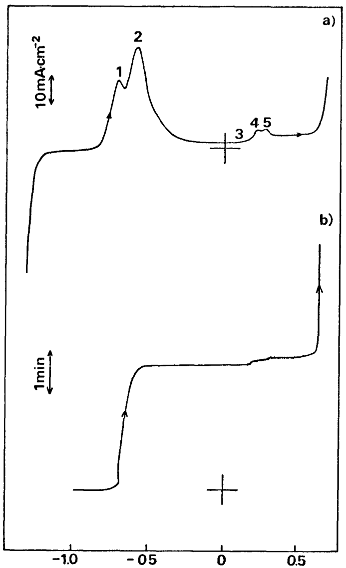

Fig. 6. Typical linear potential sweep voltammogram and chronopotentiogram on Co electrode in 6 M KOH at N_2 atmosphere at 25 °C. a) Linear potential sweep voltammogram, 50 mV s^{-1}, b) chronopotentiogram, 4.1 mA cm^{-2}.

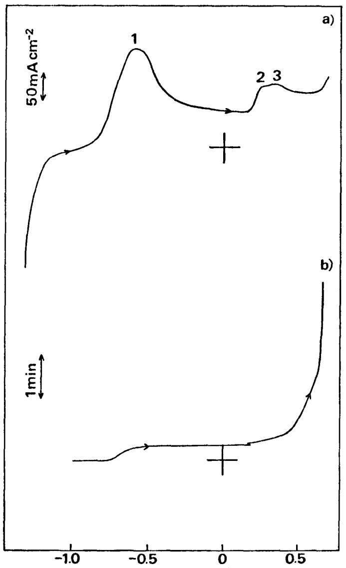

Fig. 7. Typical linear potential sweep voltammogram and chronopotentiogram on Co–B(3 : 1) sintered at the 400 °C electrode in 6 M KOH at N_2 atmosphere at 25 °C. a) Linear potential sweep voltammogram, 50 mV s^{-1}, b) chronopotentiogram, 37.7 mA cm^{-2}.

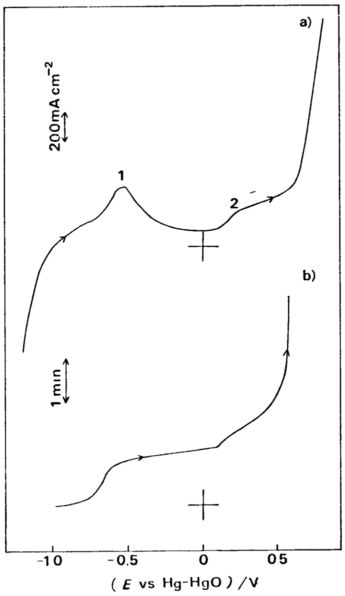

Fig. 8. Typical linear potential sweep voltammogram and chronopotentiogram on Co-Fe-B(1 : 2 : 1) sintered at the 450 °C electrode in 6 M KOH atmosphere at 25 °C. a) Linear potential sweep voltammogram, $50\ \mathrm{mV\,s^{-1}}$, b) chronopotentiogram, $37.7\ \mathrm{mA\,cm^{-2}}$.

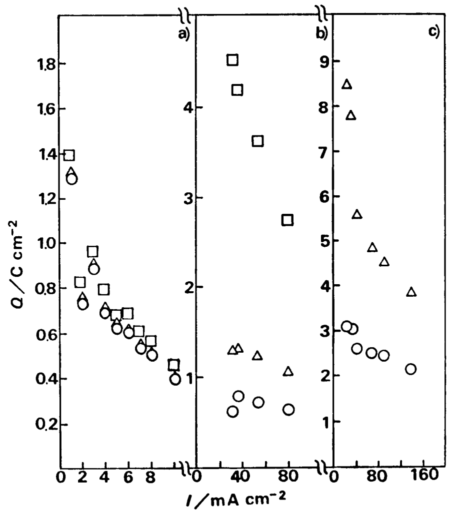

Fig. 9. Relation between amount of charge and current density at chronopotentiometry. a) Co, b) Co-B(3 : 1) sintered at 400 °C, c) Co-Fe-B(1 : 2 : 1) sintered at 450 °C. ○: 1st wave, △: 2nd wave, □: 3rd wave, where the charges for the 2nd and the 3rd waves are, for convenience, calculated from the initial potential of the 1st wave.

chronopotentiograms on the most active cobalt boride and cobalt iron boride are shown in Figs. 7 and 8. The behavior of the voltammogram and chronopotentiogram on cobalt boride (3:1) shown in Fig. 7 is similar to that on cobalt; however, the current peaks in the voltammogram due to the formation of hydroxide, shown as 1, or oxides, shown as 2 and 3, in Fig. 7, become larger (*i.e.*, the unit of the current axis in the voltammogram for Co–B is five times that for Co), and the initial potential at which the hydroxide film starts to form shifts to the more cathodic side. In the case of Co–Fe–B(1:2:1) the linear potential sweep voltammogram and chronopotentiogram are also very similar to those for Co–B(3:1), and the anodic peaks due to hydroxide (shown as 1) and oxide (shown as 2 in Fig. 8) formations become very large (*i.e.*, the unit of the current axis in the voltammogram for Co–Fe–B is twenty times that for Co). The order of the potential at which the hydroxide film starts to form is as follows:

$$\text{Co-Fe-B}(1\!:\!2\!:\!1) = -1.00\ \mathrm{V},\ \text{Co-B}(3\!:\!1) = -0.93\ \mathrm{V},$$
$$\text{Co} = -0.83\ \mathrm{V}.$$

The order of the amount of charge due to hydroxide and oxide films can easily be determined by means of chronopotentiometry. Figure 9 represents the amount of charge due to the waves in the chronopotentiograms. The total charges due to hydroxide and oxide film formations on the borides are much larger than on cobalt. Moreover, the charge due to oxide formation in the case of cobalt is much smaller than that due to hydroxide formation (*cf.* Fig. 9(a)), while in the case of borides, the charge due to the oxide formation is much larger than that of hydroxide film formation. Therefore on the borides, the hydroxide film may change completely to oxide films on the anodic side and the thicker oxide films in higher oxidation states are easily formed on the surface. It may be concluded from the above results that the composite cobalt boride and the cobalt boride with the higher activity of the oxygen evolution reaction form the thicker and more stable oxide films in higher oxidation states in which the oxygen evolution reaction occurs. The very thick oxide layer in higher oxidation states might act as an intermediate in accelerating the oxygen evolution reaction on the borides. The above conclusion corresponds fairly well with the information, deduced from the relation between the magnetic moment, μ_B, and its activity, seen in Fig. 5, considering that the formation of oxide films becomes easier with the increase in the number of unpaired valence electrons.

Therefore, the oxide films on composite cobalt borides are considered to play an important role in the oxygen evolution reaction, and it may be concluded that the ease and stability of more highly oxidized oxide film formation are strongly connected with the activity of the oxygen evolution reaction.

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