Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information for

Electrodeposition of FeCrNi stainless steel: Microstructural changes induced by anode reactions

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Cathode reactions. In order to investigate the cathode reactions in the FeCrNi electroplating bath, a series of cyclic voltammetry was performed on a Pt disk electrode. For each measurement, the electrode potential is firstly scanned in the positive direction from an open circuit potential (OCP), which is around +0.45V vs. SCE, to a given positive vertex potential, where the scan direction is reversed. Subsequently the potential is scanned to a negative vertex potential, followed by a further scan in the positive direction to the OCP. The scan rate was set at 50 mV/s. The potential sweep was performed typically three cycles for each condition. Fig. S1 shows the cyclic voltammograms (CVs) showing reactions on a Pt electrode in the FeCrNi bath along with the Base electrolyte and a simple sulfuric acid solution. The pH value of all test solutions was set at 1 which is same as that of the FeCrNi electroplating.

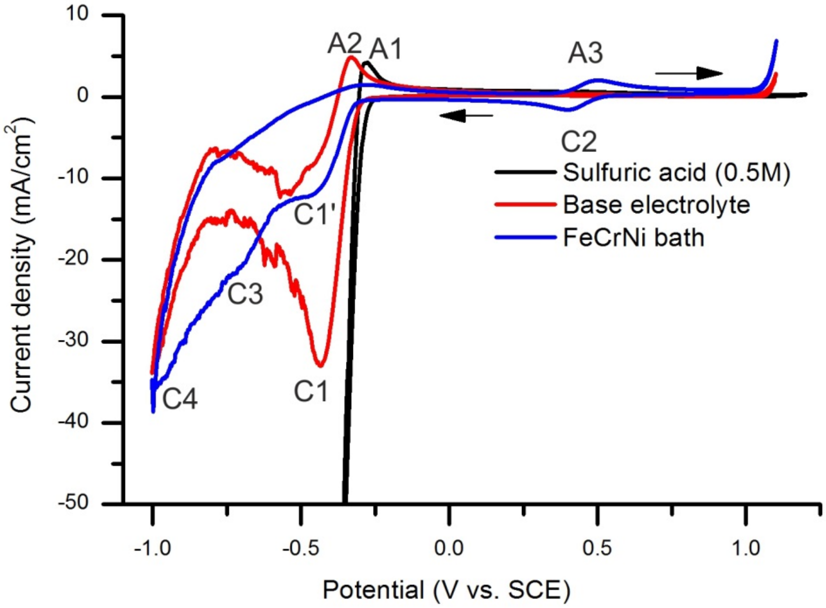

Fig. S1. Cathode reactions in FeCrNi plating bath on a Pt disk electrode (scan rate: 50mV/s).

Cyclic voltammetry in a sulfuric acid solution shows an increase of cathodic current due to hydrogen evolution at -0.25 V and an anode wave (A1) due to the reduction of adsorbed hydrogen at a similar potential in a subsequent scan in the positive direction. For the Base electrolyte, the measurement revealed a cathode wave at -0.43V (C1) as well as a subsequent sharp increase in the cathodic current from -0.8 V, which is attributed to hydrogen evolution, which is shifted to a more negative potential compared to that in a sulfuric acid solution. The anode wave at -0.43 V (C1) is thought to be associated with a reduction reaction of one of constituents in the Base electrolyte. The subsequent potential scan in the positive direction showed an anodic wave (A2), which is considered to be the anode reaction corresponding to the cathode reaction at -0.43 V (C1). The CV in the FeCrNi bath showed more cathodic and anodic waves which are attributed to the reactions of metal ions. Anodic and cathodic waves around +0.5 V (A3 and C2) correspond to the oxidation and reduction of ferrous and ferric ions. A continuous increase of the cathodic current was observed from -0.3 V to -1.0 V with some visible shoulders at -0.43 V (C1'), -0.70 V (C3), and -0.95 V (C4). The cathodic wave C1' is attributed to the same reaction as the one observed in the Base electrolyte (the cathodic wave C1), and therefore this is considered not to be directly related to the deposition reaction of metal ions. On the other hand, the cathodic waves at -0.70 V (C3) and -0.95 V (C4) which were not observed in the CV in the Base electrolyte are attributed to the reduction of metal ions such as Ni^{2+} and Fe^{2+} ions to metal films or the reduction of Cr^{3+} ions to Cr^{2+} ions.

Comparison of CVs in the FeCrNi bath performed in various potential ranges provides a further insight into the reduction reactions of metal ions. Fig. S2 shows the CVs performed in the FeCrNi bath with a potential scan between various negative vertex potentials (-0.4 V to -1.3 V) and a fixed positive vertex potential of +1.2 V. With a negative vertex potential of -0.7 V or less, CVs from different scan cycles (the first to third cycles) were almost overlapped each other (Fig. S2a-c). However, when the potential was swept to -1.0 V, which is a potential more negative than the potentials of the cathodic waves C3 and C4, the cathode wave of -0.5V (C1') became smaller after the first scan cycle, while those of the second and third cycles were essentially identical each other. This suggests that the Pt electrode surface changed during the first cycle. This might be related to the reduction of metal ions although we did not observe any difference in anodic reaction in the CV in this potential range.

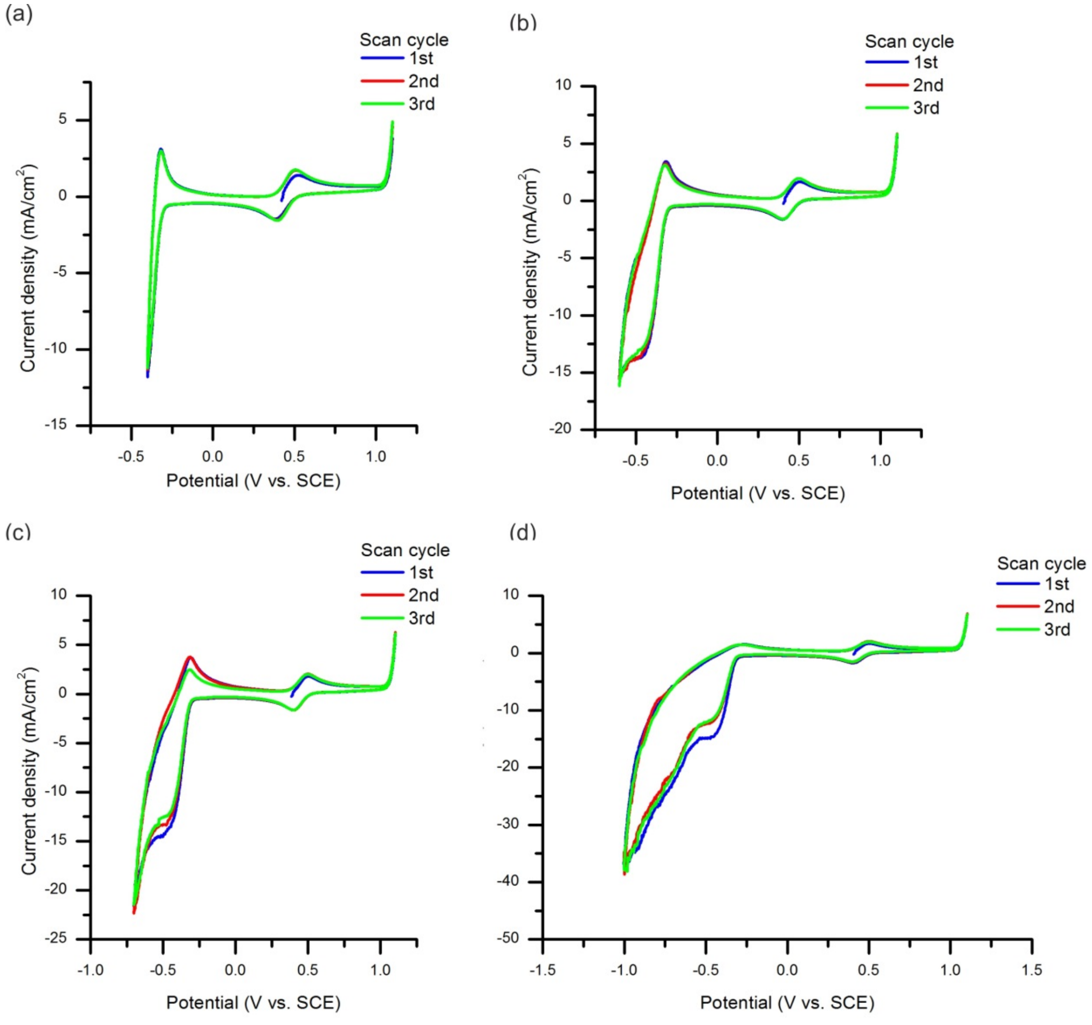

Fig. S2. Cyclic voltammetry in FeCrNi bath on a Pt disk electrode performed in various potential ranges (scan rate: 50mV/s).

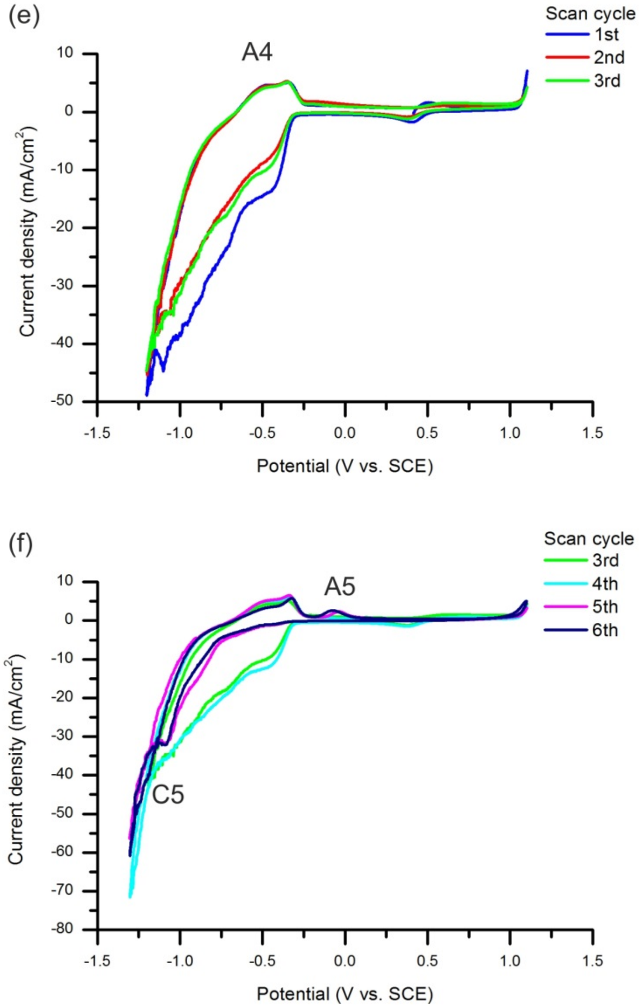

Fig. S2 (continued). Cyclic voltammetry in FeCrNi bath on a Pt disk electrode performed in various potential ranges (scan rate: 50mV/s).

A further potential sweep to -1.2 V revealed a new anodic wave at -0.5 V (A4) which is attributed to the oxidation of the metal deposits, showing that metal deposition occurs in this potential range. We also observed a clear difference between a CV of the first cycle and those of the subsequent cycles. The cathodic current from -0.3 V to -1.2 V became smaller after the first cycle, whereas the CVs of the second and third cycles were similar to each other. Furthermore, the redox reaction waves of ferric and ferrous ions (at around +0.5 V) in the CVs of the second and third cycles became much smaller than those in the CV of the first cycle. These results show that the surface chemistry of the Pt electrode significantly changed during the first scan cycle, suggesting that Pt was covered with metal deposits (probably Fe-Ni alloy) during a potential sweep at cathodic potentials. Immediately after recording the third-cycle CV between +0.2 V and -1.2 V (Fig. S3e), CVs of the fourth to sixth cycles were measured with a more negative vertex potential of -1.3 V (Fig, S2f). In these CVs, a more significant difference was observed between the fourth and the subsequent cycles, whereas that of the fourth cycle is similar to the third cycle. In the CVs from the fifth and sixth cycles, all the cathodic waves were much smaller than those for the fourth cycle. Moreover, a new cathodic peak at -1.1 V (C5) as well as a small anodic wave at around -0.06

V (A5) clearly appeared in these CVs. The cathodic peak C5 may be due to the reduction of chromium ions, while the anodic peak A5 is attributed to the formation of chromium oxide. Although the cyclic voltammetry study provides us some important insights into the cathodic reactions in FeCrNi electroplating bath, further investigation of this system seems to be difficult by simple cyclic voltammetry because of the hydrogen evolution as well as the reaction of some bath constituent in the base electrolyte, which overlaps with the reduction of metal ions.