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Synthesis of Monolayer and Bilayer of Cobalt Oxyhydrates (Na,K)x(H2O)yCoO2-δ

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Abstract

Potassium sodium cobalt oxyhydrates (Na,K)x(H2O)yCoO2− δ were synthesized from γ-Na0.7CoO2 by using aqueous KMnO4 solution in a one-pot process. Chemical and structural analyses revealed that a partial or even almost complete replacement of K+ for Na+ in the alkaline layers occurs. Direct formation of the c ≈ 13.9 Å phase is apparently associated with the larger size of K+ (1.4 Å) as compared to Na+ (1.0 Å). Formation of (Na,K) x (H2O) y CoO2− δ not only involves de-intercalation, oxidation and hydration processes, but also an ion exchange reaction. Based on a systematic study, the phase formation of (Na,K) x (H2O) y CoO2− δ with c ≈ 19.6 Å is a slow process, particularly when using aqueous KMnO4 solution with low molar ratio of KMnO4/Na. When comparing the Co K-edge X-ray absorption spectra of (Na,K) x (H2O) y CoO2− δ with those of Na x (H2O) y CoO2 obtained from Br2/CH3CN solution, the edge energy of the main peak of the bilayered hydrate is found to be 3.5 eV higher than that of the monolayered hydrate for (Na,K) x (H2O) y CoO2− δ. In contrast, the edge energy of the main peak of the bilayered hydrate is 0.4 eV lower than that of the monolayered hydrate for Na x (H2O) y CoO2. In addition, the hydration behavior of monolayered of (Na,K) x (H2O) y CoO2− δ is different from that of Na x (H2O) y CoO2. These results seem to suggest that they are two different systems.

Key words：Layered oxides; Phase transformation; Thermogravimetric analysis; X-ray spectroscopy; XRD