Supplementary material

For Li/Li⁺/Li_x M_aX_b cell with cathode material presenting rigid-band structure and for which the concentration of charge carriers in the cathode material is determined by the concentration of intercalated lithium ions, one can demonstrate the relation between the change of the cell's electromotive force and the position of the Fermi level in the cathode material. The electromotive force E of Li/Li⁺/Li_x M_aX_b cell is the difference in the chemical potential of lithium between cathode and anode (metallic Li) materials:

$$\mu_{\text{Li(cathode)}} - \mu_{\text{Li(anode)}} = -F \cdot E \tag{1}$$

If the potential of the anode is constant, the variations of electromotive force E can be ascribed to the changes of the $\mu_{\text{Li}(\text{cathode})}$, i.e. $-F \cdot \Delta E = \Delta \mu_{\text{Li}(\text{cathode})}$. Value of the chemical potential of lithium in the cathode material can be written as a sum of chemical potentials of lithium ion and electron:

$$\mu_{\text{Li(cathode)}} = \mu_{\text{Li}}^{\dagger} + \mu_{\text{e}}$$
⁽²⁾

It is known that the chemical potential of lithium ion in the cathode material can be expressed as:

$$\mu_{Li}^{+} = \mu^{o}_{Li}^{+} + k_{B}T \cdot \ln[Li^{+}]$$
(3)

then:

$$\Delta \mu_{\text{Li}}^{+} = k_{\text{B}} \mathbf{T} \cdot \ln \qquad \frac{[Li^{+}]_{f}}{[Li^{+}]_{i}} \tag{4}$$

where *f* and *i* denote the final and initial states, respectively.

Chemical potential of electrons in the cathode material can be identified as the energy of the Fermi level, which changes are determined by the electronic structure (DOS function) in the vicinity of E_F , and can vary in the range of 1 eV or more (roughly of the

order of band width) upon introduction of electrons during lithium intercalation. For the change of lithium ions concentration of the order of 1 mole ($\Delta [\text{Li}^+] \sim 1$), the change of chemical potential of lithium ions in the cathode material $\Delta \mu_{\text{Li}}^+$ is of the order of $k_B T$, i.e. 0.025 eV at room temperature (eq. 5), while the change of the chemical potential of electrons in the cathode material is two orders of magnitude higher ($\Delta \mu_{\text{Li}}^+ \ll \Delta \mu_e$). Therefore, variations of the electromotive force of the Li/Li⁺/Li_xM_aX_b cell, which accompany the intercalation reaction, correspond mainly to those of the chemical potential of the about by the alkaline metal doping.

Similar reasoning, yielding the same scientific conclusions, may be shown for $Na/Na^{+}/Na_{x}M_{a}X_{b}$ cell.

XRD pattern of "as synthesized" sodium cobaltate powder is depicted in Fig. 11. Surface morphology of the obtained Na_{0.69}CoO_{2-y} and Na_{0.72}CoO_{2-y} powders are presented in Fig. 12. The average size of particles was found to be about 6 μ m. Na_xCoO₂ exhibits wellcrystallized platelet-like grains, exposing flat surfaces with easily noticeable hexagonal shape. Bright field TEM images and EDX analysis are presented in Figs. 13. Voltammetry studies performed for slow scanning rates (0.1 and 0.05 mV·s⁻¹) are shown in Fig. 14. Additional results of current rate influence on the electrochemical behavior of Na/Na⁺/Na_xCoO_{2-y} cells, as recorded during discharge for currents in C/50 to 1C range, are presented in Fig. 15.

Figures

Fig. 11 XRD pattern with Rietveld refinement for the synthesized Na_{0.72}CoO_{2-y}.

Fig. 12 SEM images of $Na_{0.69}CoO_{2-y}$ powder with: (a) 1000x and (b) 5000x magnification and $Na_{0.72}CoO_2$ powder with: (c) 1000x and (d) 5000x magnification.

Fig 13 STEM-HAADF images of cross-sectioned particle and corresponding EDS results performed in the marked place.

Fig. 14 Voltammetry studies for 2^{nd} cycle results of 0.05 and 0.1 mV·s⁻¹ rates for Na/Na⁺/Na_xCoO₂ cell.

Fig. 15 Discharge curves of Na/Na⁺/Na_xCoO₂ cells measured for C/50-1C current range.

Computational details

Electronic structure of ordered compounds Na_xCoO_2 with x=0, 1/2 and 1 resulted from *ab initio* band structure calculations by the fully charge self-consistent Korringa–Kohn–Rostoker (KKR) technique. We used the full-potential KKR method, whose formalism has been widely discussed by many authors [1] with technical details shown in reference [2]. In our computations the novel quasilinear algorithm [3] was implemented. The full form of crystal potential was used over the whole atomic Voronor[•] cells, with *l* truncation on each atom up to $l_{max} = 3$. Within the local density approximation (LDA), the Perdew-Wang formula for the exchange-correlation part of the crystal potential was employed. For the crystal potentials converged below ~1 meV, total, site-decomposed and *l*-decomposed density of states (DOS) were computed. The Fermi level E_F was precisely determined from the Lloyd formula [4], which appears to be particularly important in systems close to magnetic or metal-semiconductor instability.

To account for chemical disorder (O and Na vacancy defects) in Na_xCoO_{2-y} alloys, the coherent potential approximation (CPA) was incorporated into the KKR technique. In KKR-CPA calculations the crystal potential of *muffin-tin* was converged selfconsistently for all atoms, including a vacancy, except for an assumption of no nuclear charge (Z = 0) in the latter (see, e.g. [5]). Like in KKR calculations of ordered systems, the Fermi energy in disordered alloys was determined precisely (~1 meV) via the generalized Lloyd formula [4] using an elliptic contour in the complex energy plane. The KKR-CPA Green function was computed on a mesh of approximately 500 special k-points in the irreducible part of the Brillouin zone. The self-consistency cycles were repeated until input-output differences of the potentials and charges inside the muffin-tin spheres were of the order of 5-10 meV and $10^{-3} e$ (*e* - electron charge), respectively. More theoretical details can be found in Ref. [6].

In all figures presented here, E_F is located at zero, and DOS curves are given in eV^{-1} per spin direction.

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