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Short communication

Comparative study of $LiCoO_2$ surface modified with different oxides

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Abstract

It has been shown that crystal and local structure of $LiCoO_2$ does not noticeably change after surface modification with different inert oxides (MgO, $Li_2O{\cdot}2B_2O_3$, Al_2O_3, ZnO, ZrO_2) using wet chemical method. However, in the case of $LiCoO_2/Al_2O_3$, a small amount of Co_3O_4 phase was observed. Chemical delithiation study shows better structural and chemical stability of $LiCoO_2/Al_2O_3$ under treatment in water and acid solutions. Surface modification, despite of oxide, leads to improved cyclability in the 3–4.5 V range and to enlarged rechargeable capacity up to 175 mAh g^{-1}. The capacity increases in the row $ZnO \sim Al_2O_3 > Li_2O{\cdot}2B_2O_3 > ZrO_2 > MgO >$ bare $LiCoO_2$. On the other hand, $LiCoO_2$ treated with ethanol without salts also shows improved capacity retention. According to $-dQ/dU = f(U)$ curves, phase transitions of $LiCoO_2$ during charge–discharge are not suppressed. It is concluded that surface modification results both in nanoparticlate shell with suitable electronic and ionic conductivity formation and in surface stabilization via inhibiting surface active centers.
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Keywords: $LiCoO_2$; Surface modification; Inert oxides; Acid treatment; Electrochemical testing up to 4.5 V; Enlarged capacity; Improved cyclability

1. Introduction

The electrochemical cycling of $LiCoO_2$ at a high cutoff voltage results in a significant deterioration of the stability of the cathode. It is believed that capacity loss is related to non-uniform structural changes and an increase of cobalt dissolution in the electrolyte. According to Aurbach et al. [1], capacity loss of $LiCoO_2$ electrodes is due to formation of surface films which electronically isolate the particles from each other and current collector. Substantial efforts have been made to increase the specific capacity of $LiCoO_2$ by utilizing a higher upper cutoff potential, without sacrificing capacity retention. Surface modification of $LiCoO_2$ with different oxides, such as ZrO_2 [2,3], Al_2O_3 [3–9], MgO [5,10], ZnO [11], TiO_2 [12], etc. is widely studied to avoid the unwanted surface reactions and to protect the bulk. This method changes the surface properties of cathode materials. Although various types of coatings have demonstrated the significant improvements in capacity retention, the mechanism of capacity fading at high voltage and the effects of surface coating is far from clear. Cho and co-workers [2,4] believe that the coating layer serves as a mechanical barrier to prevent the Li_xCoO_2 lattice from expanding and contracting during charge/discharge cycling. They showed that $LiCoO_2$ coated with oxides with larger fracture toughness have better stability of the *c*-axis dimension and better cycling behavior. The fracture toughness of the oxides decreases in the order $ZrO_2 > Al_2O_3 > TiO_2 > B_2O_3 > SiO_2$. The best effectiveness of ZrO_2 surface coating was attributed to the whole suppression of the variation of the *c* value of $LiCoO_2$—'zero-strain' material.

However, Chen and Dahn [3] reported that poor cyclability of $LiCoO_2$ at high voltage is mainly caused by two factors. One is that some chemical species decomposed between 4.2 and 4.5 V, and the other is due to side reactions between the cathode and electrolyte, resulting in growth of a high impedance layer on the surface of $LiCoO_2$. Coating does not suppress the lattice expansion and phase transition of $LiCoO_2$ during charge–discharge, but it could change its surface properties. They discovered that the capacity degradation could be retarded by grinding or heating the $LiCoO_2$ powders to produce some fresh surfaces.

The authors [7] proposed that the Al_2O_3 coating on the surface of $LiCoO_2$ may form some type of protection layer to cover the active centers which serve as catalyst sites for the electrolyte decomposition. In [11], the reasons of cyclability promotion by ZnO coating were discussed from the viewpoint of microstructural evolution before and after cycling. After coating, newly produced nanoparticles form on the smooth surfaces

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Table 1
Decomposition temperature of precursors

Precursor	Decomposition reaction	T_{dec} (°C)
$Mg(CH_3COO)_2$	$Mg(CH_3COO)_2 + 4O_2 \rightarrow MgO + 3H_2O + 4CO_2$	320
H_3BO_3	$2H_3BO_3 \rightarrow B_2O_3 + 3H_2O$	185
$Al(OH)_3$	$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$	600
$Zn(CH_3COO)_2$	$Zn(CH_3COO)_2 + 4O_2 \rightarrow ZnO + 3H_2O + 4CO_2$	240
$ZrO(NO_3)_2 \cdot 2H_2O$	$ZrO(NO_3)_2 \cdot 2H_2O \rightarrow ZrO_2 + 2H_2O + 2NO_2 + 1/2O_2$	300

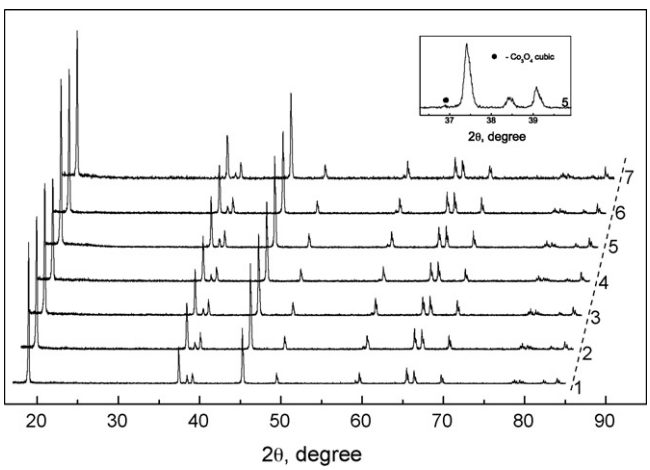

Fig. 1. X-Ray patterns of bare (1) and surface modified $LiCoO_2$: MgO (2), ZnO (3), $Li_2O{\cdot}2B_2O_3$ (4), Al_2O_3 (5), ZrO_2 (6) and treated with ethanol (7). Inset shows zoomed curve (5).

of bare $LiCoO_2$. These nanoparticles gather on some specific planes (probably containing some residual anions, e.g., CO_3^{2-}) rather than uniformly disperse on the surfaces, while planes of other orientations remain smooth and free of nanoparticles. These anions attract a large portion of the Zn^{2+} cations to deposit on these planes as $LiCoO_2$ ages in the coating solution.

Surface chemistry is of extreme importance for high-dispersed cathode materials. The aim of the present study was to perform a comparative study of structure and properties of $LiCoO_2$ prepared by mechanical activation and surface modified with different inert oxides (MgO, $Li_2O{\cdot}2B_2O_3$, Al_2O_3, ZnO, ZrO_2) by wet chemical method and treated with ethanol.

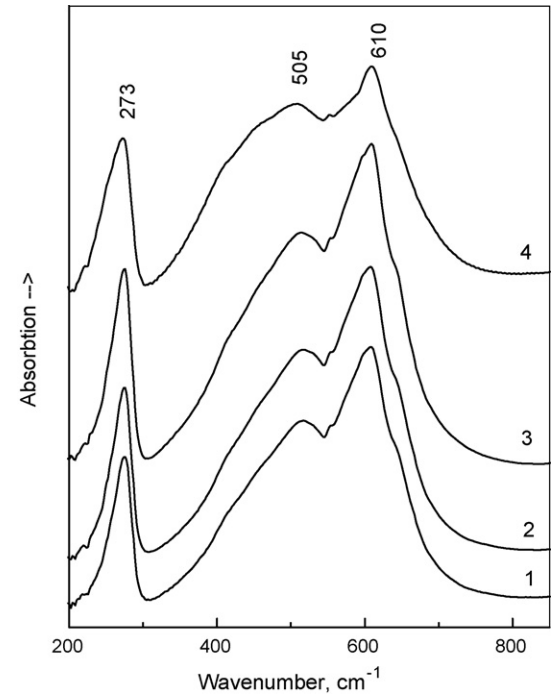

Fig. 2. IR spectra of bare (1) and surface modified $LiCoO_2$: MgO (2), $Li_2O{\cdot}2B_2O_3$ (3), Al_2O_3 (4).

2. Experimental

$LiCoO_2$ was prepared by preliminary mechanical activation of the Co_3O_4 + LiOH mixture in high-energetic planetary mill followed by subsequent short heat-treatment at 800 °C. To obtain ∼ 0.5–4% surface coating by MgO, ZnO, $Li_2O{\cdot}2B_2O_3$, ZrO_2 and Al_2O_3, as prepared $LiCoO_2$ was mixed with ethanol solutions of Mg or Zn acetates; water solutions of $ZrO(NO_3)_2{\cdot}2H_2O$; mixtures of LiOH + H_3BO_3 and $Al_2(SO_4)_3 + Na_2CO_3$ by magnetic stirring for 30 min. Then, the $LiCoO_2$ powder was separated from the coating solutions by centrifugation and dried at 80 °C. Finally, the samples were heated at 400–600 °C for 4 h in air. Experimental temperature was chosen based on $T_{dec.}$ of precursors (see Table 1) which does not exceed 600 °C.

Crystal and local structure of as prepared materials was studied by X-ray powder diffraction (DRON-3M diffractometer, Cu Kα radiation) and IR spectroscopy (Bruker FTIR spectrometer, pellets with CsI, 200–4000 cm^{-1}). Picknometric density was measured by standard procedure in toluene. The microstructure

Table 2
Cell parameters for surface modified $LiCoO_2$

Inert oxide	Lattice constants (Å)		c/a	V (Å^3)	I_{003}/I_{104}
	a	c			
$LiCoO_2$, initial	2.8152 ± 0.0003	14.048 ± 0.001	4.990	96.4206	1.73
MgO	2.8152 ± 0.0001	14.050 ± 0.001	4.991	96.4354	1.54
ZnO	2.8147 ± 0.0003	14.047 ± 0.002	4.990	96.3745	1.61
$Li_2O{\cdot}2B_2O_3$	2.8150 ± 0.0002	14.051 ± 0.001	4.991	96.4248	1.29
Al_2O_3	2.8152 ± 0.0002	14.049 ± 0.001	4.990	96.4226	1.50
ZrO_2	2.8150 ± 0.0002	14.048 ± 0.001	4.990	96.4050	1.76
Ethanol	2.8146 ± 0.0002	14.048 ± 0.001	4.991	96.3740	1.72

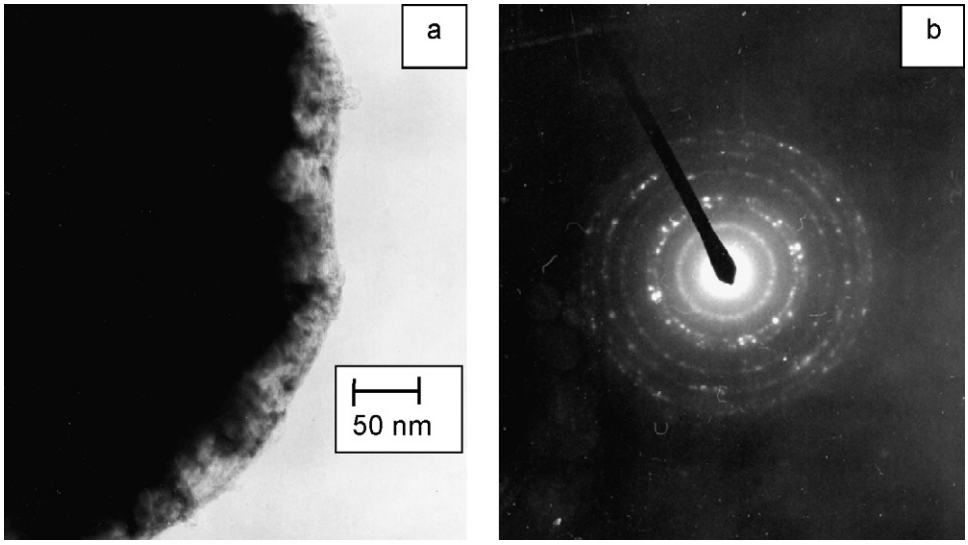

Fig. 3. TEM image (a) and electron diffraction (b) of and $LiCoO_2$ surface modified with Al_2O_3.

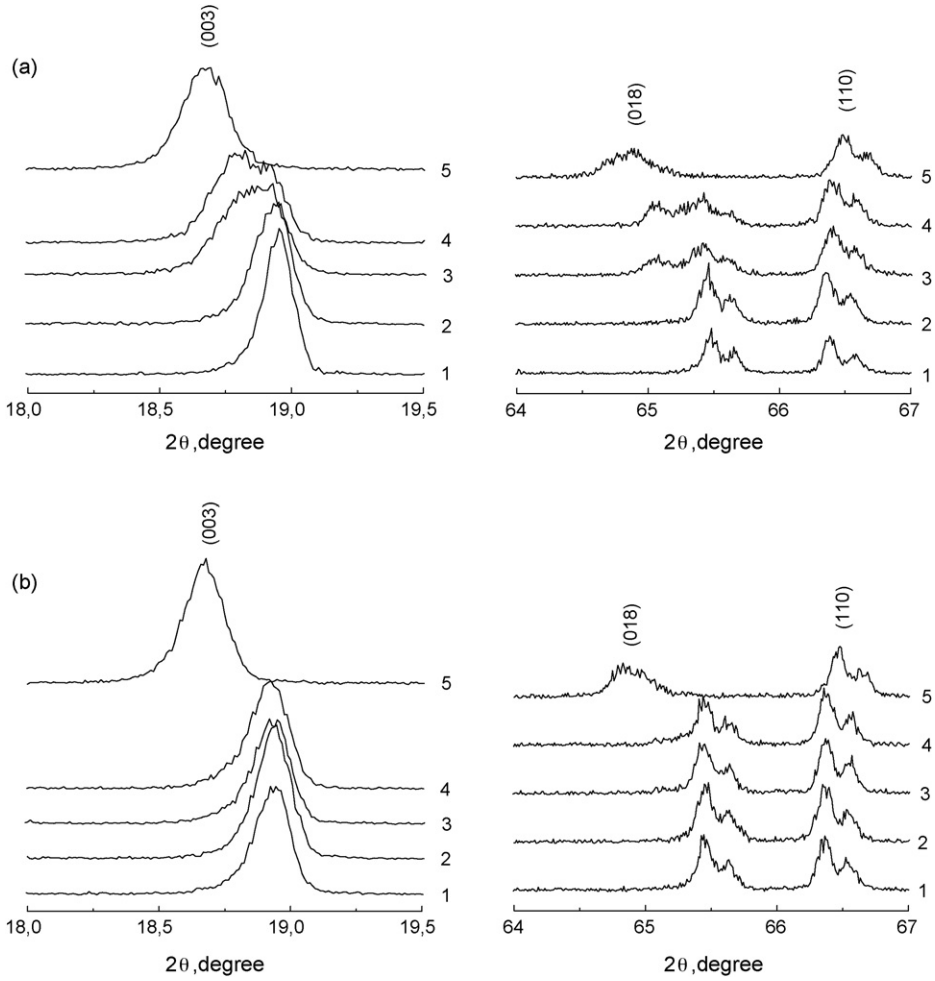

Fig. 4. X-Ray patterns of bare $LiCoO_2$ (a) and $LiCoO_2$ surface modified with Al_2O_3 (b) after treatment with H_2O and H_2SO_4: 1, untreated; 2, H_2O; 3, 0.05N H_2SO_4; 4, 0.1N H_2SO_4; 5, 1N H_2SO_4.

Table 3
Chemical analysis data of $LiCoO_2$ and $LiCoO_2/Al_2O_3$ treated with H_2O and H_2SO_4

Sample	Treatment	Li (% to theoretical)		Co (% to theoretical)		Li/Co ratio in solid	Cell parameters	
		In filtrate	In solid	In filtrate	In solid		*a* (Å)	*c* (Å)
$LiCoO_2$ bare	H_2O	0.4	99.6	0	100	$Li_{0.996}Co_{1.000}$	2.8152 (3)	14.047 (1)
	0.1N H_2SO_4	21.2	78.8	13.3	86.7	$Li_{0.788}Co_{0.867}$	2.814 (1) (first phase) 2.8133 (3) (second phase)	14.060 (5) (first phase) 14.167 (2) (second phase)
	1N H_2SO_4	56.4	43.6	33.2	66.8	$Li_{0.436}Co_{0.668}$	2.811 (1)	14.24 (1)
$LiCoO_2/Al_2O_3$	H_2O	0.3	99.7	0	100	$Li_{0.997}Co_{1.000}$	2.8150 (2)	14.048 (1)
	0.1N H_2SO_4	8.2	91.8	4.5	95.5	$Li_{0.918}Co_{0.955}$	2.8148 (4)	14.050 (2)
	1N H_2SO_4	49.3	50.7	21.8	78.2	$Li_{0.507}Co_{0.782}$	2.8112 (5)	14.245 (3)

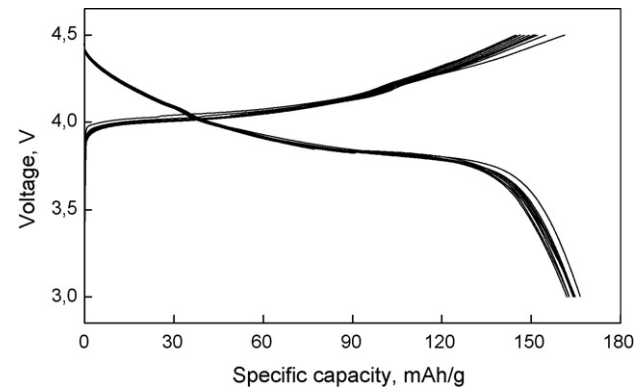

Fig. 5. Charge–discharge curves for $LiCoO_2$ surface modified with Al_2O_3.

was examined by a JEOL JEM-2000FX high- resolution transmission electron microscope. Chemical and structural stability of materials was studied by treatment with distilled water (pH 5.5) and water solutions of H_2SO_4 (0.05; 0.1 and 1N). Chemical analysis of delithiated samples was carried out by atomic absorption spectroscopy and flame photometry. Electrochemical tests were performed in laboratory cells with the $LiPF_6$ + EC + DMC electrolyte and Li anode in the 3–4.5 V range at C/10 rate and $T = 20\,^{\circ}C$. Cathodes were prepared by mixing active material with 15% Super P (TIMCAL Ltd).

3. Results and discussion

It is seen from Fig. 1 that crystal structure of $LiCoO_2$ does not noticeably change after surface modification indicating that most coating oxides are either amorphous or nanoparticulate, or form solid solution at the particle surface. However, small reflections of ZnO and Co_3O_4 are present on the XRD patterns of $LiCoO_2$ surface modified with ZnO and Al_2O_3, respectively. The appearance of tiny amount of Co_3O_4 phase in Al_2O_3-modified $LiCoO_2$ can be a result of the following possible surface interaction

$$LiCoO_2 + (x/2)Al_2O_3 \rightarrow LiCo_{1-x}Al_xO_2 + (x/3)Co_3O_4 + (x/12)O_2.$$

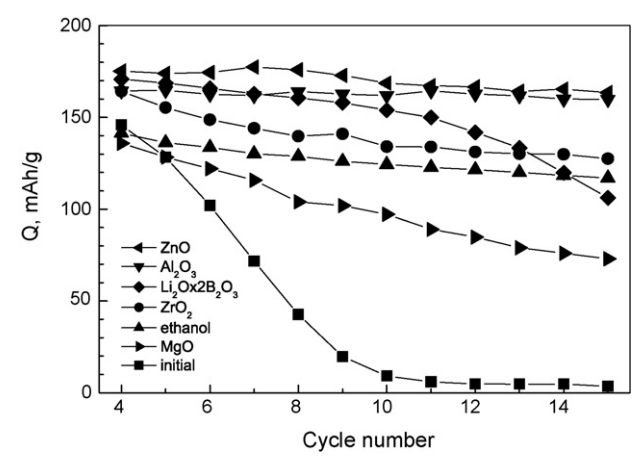

Fig. 6. Discharge capacity of bare and surface modified $LiCoO_2$ vs. cycle number.

The calculated cell parameters of coated samples show no detectable changes after coating evidencing that the particle bulk is free from Me-dopants. (Table 2). In the IR spectra of surface modified samples, the form and the position of LiO_6 and CoO_6 lines retain (Fig. 2), i.e. the local structure does not noticeably change as well.

However, picknometric measurements show that density increases from 4.522 g cm^{-3} for bare $LiCoO_2$ to 4.881 and 4.963 g cm^{-3} for $LiCoO_2$ treated with ethanol and surface modified with Al_2O_3, respectively.

TEM study demonstrates the formation of polycrystalline surface layer on the crystalline surface of $LiCoO_2$ particles (Fig. 3). It has been noticed that at low concentrations, the coating is uniform. The coating layer is about 30 nm. However, at high coating level, loosely held agglomerates of the coating material were found glued to the surface, which suggests that its amount is more than required to form a uniform coating on the cathode powder. It is also possible that during the calcinations process, some of the coating species might have diffused into the bulk, resulting in the formation of solid solutions and making the coating more adherent.

Indeed, the Al 2s XPS spectrum of Al_2O_3-modified $LiCoO_2$ (not shown here) indicates that the surface is enriched with Al [13]. The binding energy of Al 2s differs from that of α-Al_2O_3, pointing Al ions to present in disordered coordination. Al concentration sharply decreases after Ar etching: Al/Co ratio changes from 2.9 to 0.34. Thus, Al is concentrated in the surface and near-surface layer.

Chemical and structural stability of $LiCoO_2$ surface modified with Al_2O_3 was studied by chemical delithiation using distilled water (pH 5.5) and water solutions of H_2SO_4 (0.05, 0.1, 1N). The samples were treated by magnetic stirring for 1 h. Different changes on X-ray patterns of chemically delithiated $LiCoO_2$ with and without surface modification are observed (Fig. 4). The 0 0 3, 0 1 8 and 1 1 0 reflections on the patterns of bare $LiCoO_2$ shift starting from dilute acid solutions, whereas for Al_2O_3 modified sample, they retain up to strong acid solution. Cell parameters (Table 3) evidence two-phase domain formation for bare $LiCoO_2$ and only one-phase for the coated sample treated with 0.1 N H_2SO_4. Note, Cho et al. observed a slight variation of the lattice constant *a* during electrochemical charging in both the bare and coated $Li_{1-x}CoO_2$, whereas variation of constant *c* was much lower for the coated samples. According to chemical analysis of filtrates, water treatment of both samples brings to a slight extraction of Li only. Under acid treatment, both Li and Co are dissolved; however, their amounts are lower in the case of coated material. Thus the coating retard the dissolution of Co. We did not observe a noticeable change in pH value during ethanol treatment of $LiCoO_2$ indicating the absence of Li extraction, contrary to results of [11] for Li extraction in methanol.

Electrochemical cycling studies show significant increase of discharge capacity and improved cyclability (Figs. 5 and 6). When cycled to 4.5 V, bare $LiCoO_2$ has an initial capacity of about 170 mAh g^{-1}. However, without coating, the capacity fades quickly during cycling. $LiCoO_2$ coated with ZnO and Al_2O_3 delivers a capacity of about 170–175 mAh g^{-1} with an excellent cycling behavior. This improvement leads to about 30% increase of specific capacity of $LiCoO_2$ when charged only to 4.2 V. An increase of capacity was observed for the coated samples at the first cycles with different cutoff voltage: 4.2, 4.3 and 4.5 V (not shown here). The reason is in the transformation

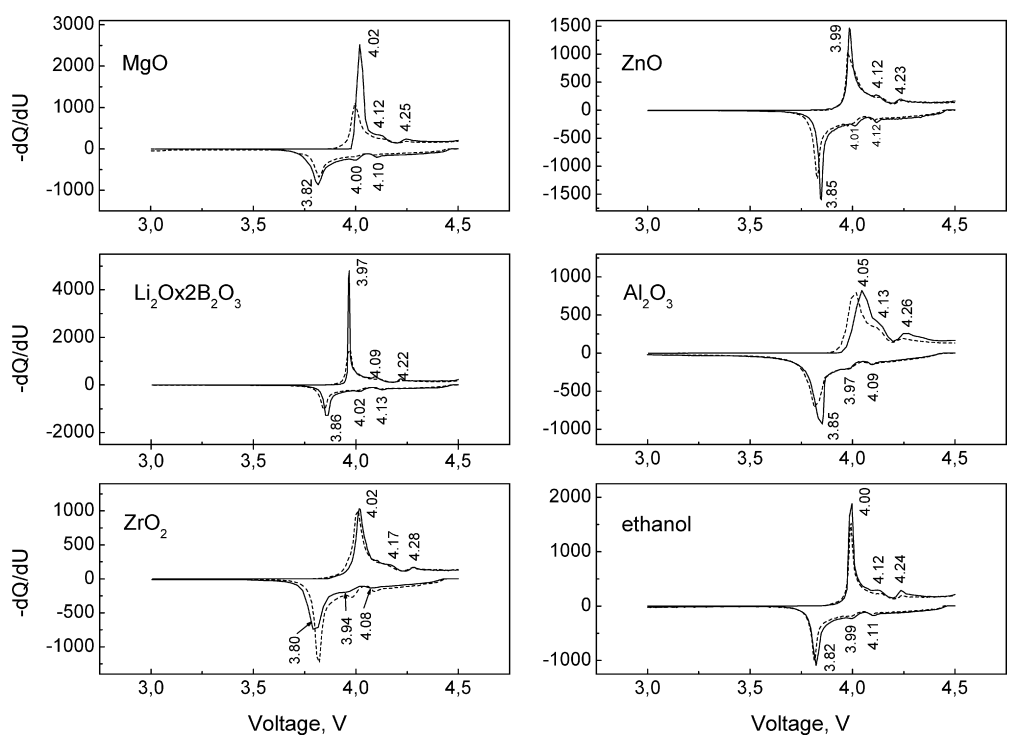

Fig. 7. Differential capacity of surface modified $LiCoO_2$ vs. potential. Solid lines—the 1st cycle; dotted lines—10th cycle.

of isolating primary coating to better ionic and electronic conductive layer. Surprisingly, that Al_2O_3-coated material shows superior properties, though X-ray diffraction indicates the presence of small amounts of inactive Co_3O_4: it is believed that capacity fading in $LiCoO_2$ is attributed to the side reactions such as the formation of Co_3O_4 upon overcharging.

On the other hand, the $LiCoO_2$ sample treated with ethanol without salts and heated at 600 °C also showed improved capacity retention as compared with bare $LiCoO_2$, but worse than surface modified materials. Ethanol treatment does not lead to surface layer formation. Probably, it acts as an inhibitor of active centers which serve as catalyst sites for the electrolyte decomposition, e.g., oxygen ions with higher value of binding energy, i.e. with smaller electronic density [14].

Fig. 7 demonstrates the differential capacity vs. cell potential for $LiCoO_2$ surface modified with different oxides for the 1st and for the tenth cycles. It is clearly seen, that all oxidation and reduction peaks retain.

It is worth noting that to achieve higher capacity and better retention, one should choose the optimized amount of coating material paying attention to specific surface area of cathode material and its morphology. The discrepancy of results obtained by different authors is also due to different coating solution and different procedure as used.

4. Conclusions

Thus, it has been shown that surface modification of $LiCoO_2$ with different inert oxides does not touch the bulk. Coating layer consists of nanoparticulate oxides or solid solutions. In the case of $LiCoO_2/Al_2O_3$, tiny amount of Co_3O_4 phase was observed. Coating improves structural and chemical stability of $LiCoO_2$ under acid delithiation. Surface modification by inert oxides leads to improvement of cyclability in the 3–4.5 V range and to increase of rechargeable capacity up to 175 mAh g^{-1}, though the phase transitions retain. On the other hand, ethanol treatment also improves $LiCoO_2$ electrochemical behavior at high cutoff voltage by diminishing active centers which served as catalyst sites for the electrolyte decomposition. Thus, the mechanism of surface treatment is nested on the improved surface chemistry.

Acknowledgements

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