



Short communication

Charge–discharge properties of LiCoO₂ electrodes modified by olivine-type compounds of LiMgPO₄ for lithium secondary batteriesHideyuki Morimoto^{a,*}, Hiroyuki Awano^b, Junpei Terashima^b, Shinji Nakanishi^b, Yasunori Hirama^a, Kiyotaka Ishikawa^a, Shin-ichi Tobishima^a^a Department of Chemistry and Chemical Biology, Graduate School of Engineering, Gunma University, 1-5-1 Tenjin-cho, Kiryu, Gunma 376-8515, Japan^b Toyota Motor Corporation, 1200, Mishuku, Susono, Shizuoka 410-1193, Japan

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ABSTRACT

Fine particles of Olivine-type LiMgPO₄ were prepared directly from a mixture of Li₂O, MgO, and P₂O₅ as starting materials using a mechanical milling technique at room temperature. LiMgPO₄ fine particles were investigated as surface modification materials of LiCoO₂ cathodes in lithium cells. Electrolytes of these cells were 1 mol dm⁻³ LiPF₆-ethylene carbonate (EC)/ethyl methyl carbonate (EMC) (3:7 volume ratio). LiMgPO₄-modified LiCoO₂ cathodes exhibited better charge–discharge performance for high charge cut-off potential of 4.5 V (vs. Li/Li⁺) in lithium cells than that of LiCoO₂ cathode. Olivine-type LiMgPO₄ may inhibit oxidative decomposition of the electrolytes on LiCoO₂ particle surface without a crystal structure change of LiCoO₂ for high charge cut-off potentials.

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1. Introduction

LiCoO₂ positive electrodes have been used in most commercial lithium ion batteries. LiCoO₂ electrodes show good cycle performance with charging voltage lower than 4.2 V. Although LiCoO₂ cathodes charged at higher voltage exceeding 4.2 V show high capacities, their capacities decrease drastically during cycling [1]. One of the reasons for capacity degradation is reported to be the decomposition of electrolyte on LiCoO₂.

LiCoO₂ modified with oxide materials such as ZrO₂ [1–5], Al₂O₃ [6–9] and MgO [10,11] have been reported to improve electrode performance. For example, LiCoO₂ modified with ZrO₂ has been reported to show better cycle performance than LiCoO₂ charged at a high voltage of 4.5 V (vs. Li/Li⁺) [1–3]. Zhaohui and J. R. Dahn have reported that ZrO₂ coating affects the lattice expansion of LiCoO₂ and ZrO₂-coated LiCoO₂ shows better cycling behavior than uncoated materials at 4.5 V charge [1]. Also olivine LiFePO₄ coated LiCoO₂ is reported to improve the cycle performance of the cathode material at charge cut-off voltage of 4.2 V at 60 °C [12]. LiCoPO₄

phase grown LiCoO₂ electrodes exhibit excellent cycle life at high working voltages [13].

In this paper, the LiMgPO₄ fine particles are investigated as coating materials of LiCoO₂ to improve cycling performance. Olivine-type structure LiMgPO₄ shows high electrochemical stability being due to the structure of PO₄ unit and transition metal free. It is expected that LiMgPO₄ fine particle work as a new buffer layer to inhibit decomposition of electrolytes on LiCoO₂ particle surface. Charge–discharge cycling behavior of LiMgPO₄-modified LiCoO₂ electrodes are investigated for charge cut-off potential of 4.5 V (vs. Li/Li⁺) in lithium cell.

2. Experimental

2.1. Preparation of LiMgPO₄

Reagent-grade Li₂O, MgO, and P₂O₅ (Wako Pure Chemical Industries, Ltd.) were used as starting materials. The mechanical milling treatment was carried out on the mixture of starting materials using a planetary ball-mill (Fritsch Corp., p-7) with a rotation speed of 450 rpm at room temperature in a dry Ar atmosphere. Stainless steel and zirconia was used as the pots and balls for planetary ball milling, respectively. The volume of

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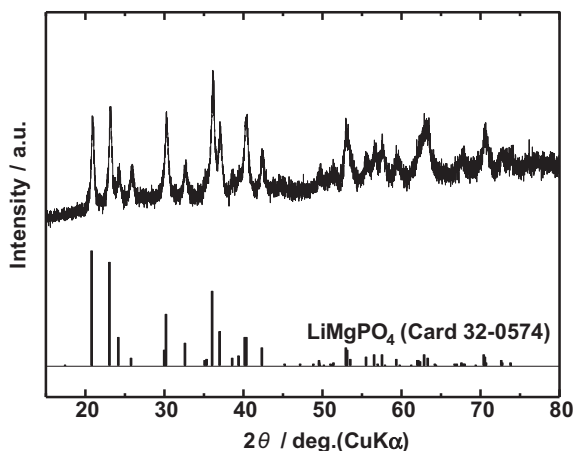


Fig. 1. X-ray diffraction pattern of a product prepared by a mechanical milling treatment of the mixture of Li_2O , MgO and P_2O_5 at room temperature.

the pots and the number of the balls were 45 mL and 10, respectively. Balls-to-mixture weight ratios ranging from 10:1 to 20:1 were employed using balls with diameters of 10 mm. X-ray diffraction measurements (Rigaku Corp., MiniFlex) with $\text{Cu K}\alpha$ radiation were performed to identify the crystalline phase of product powder obtained by mechanical milling treatment for the mixture of starting materials. Particle size and morphology was estimated by SEM (JEOL Ltd., JSM-6510) observations.

2.2. Cell preparation and electrochemical measurements

Charge–discharge measurements with a constant current density of 0.2 mA cm^{-2} during first cycle and 0.5 mA cm^{-2} from second cycle to the end cycle were carried out by using the 2032 coin cells at room temperature. These cells have a lithium metal counter electrode (Honjo chemical Corp., lithium foil of 0.5 mm thickness) and the working electrode. The working electrodes were fabricated from LiCoO_2 or mechanical milled olivine powder mixed LiCoO_2 (85 wt. %), acetylene black (5 wt.%), and polyvinylidene fluoride (PVDF, 10 wt%). In this experimental, the mechanical milled olivine powder and LiCoO_2 were manually

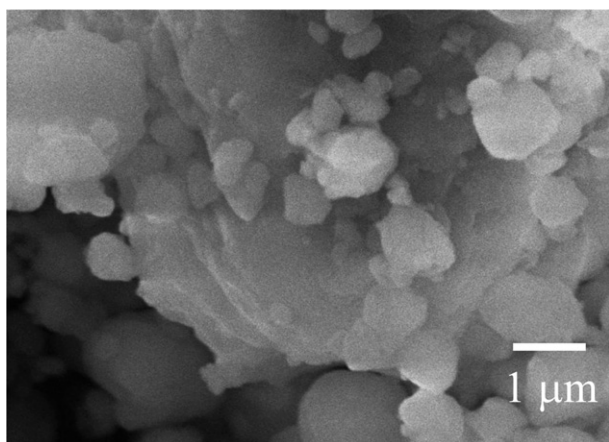


Fig. 2. SEM images of LiMgPO_4 powder prepared by mechanical milling. a) Scale: 10 μm , b) Scale: 1 μm .

mixed by using a pestle in an agate motor at room temperature. The contents of olivine powder vs. LiCoO_2 were 2, 5, 10, and 20 wt. %. Next, the mixture and acetylene black were mixed by using a pestle in agate motor. The powder was slurred with PVDF binder solution including 1-methyl-2-pyrrolidone (NMP) solvent. The slurry painted on the Al sheet of the current collector was dried at 80°C . It was pressed and dried in vacuum at 120°C . The electrolyte was 1 mol dm^{-3} LiPF_6 in mixed solvents of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) (3:7 volume ratio). The charge–discharge measurements were carried out at the cut-off potential range from 3.0 to 4.2 V and from 3.0 to 4.5 V vs. Li/Li^+ , respectively.

Liner sweep voltammetry (LSV) measurements were carried out from open potential to 8 V (vs. Li/Li^+) for a scan speed of 0.5 mV s^{-1} using electrochemical measurements system (Hokuto Denko Corp., HZ3000). Then ac impedance spectroscopy measurements for the cells were carried out by using an impedance analyzer (Ivium corp., Ivium Stat). The frequency range and applied voltage was 0.01–100 kHz and 10 mV, respectively. The electrochemical measurements were carried out at room temperature.

3. Results and discussion

Fig. 1 shows X-ray diffraction pattern of a product prepared from Li_2O , MgO and P_2O_5 by a mechanical milling treatment at room temperature. The X-ray pattern assigned to olivine-type structure LiMgPO_4 (ICDD card PDF#32-0574). This result means that LiMgPO_4 powder was prepared by mechanochemical synthesis. **Fig. 2** shows SEM images. Particle size was less than $1 \mu\text{m}$ and a part of particles were observed to aggregate. LiMgPO_4 fine powder was obtained by mechanical milling technique at room temperature. **Fig. 3** shows SEM images of the powder obtained by mixing the mechanical milled LiMgPO_4 and LiCoO_2 powder in agate motor. SEM images exhibits that LiMgPO_4 particles were scattered on the surface of LiCoO_2 particle. **Fig. 4** shows SEM images of LiCoO_2 electrode surface with and without LiMgPO_4 powder. SEM images note that LiMgPO_4 and acetylene black powder with PVDF binder modified the surface of LiCoO_2 particle.

Fig. 5 shows the discharge curves of Li/LiCoO_2 cells at 2nd cycle for charge cut-off potential of 4.2 and 4.5 V at constant current density of 0.5 mA cm^{-2} . The discharge capacity (180 mA h g^{-1}) of charge cut-off potential of 4.5 V is higher than that (133 mA h g^{-1}) of charge cut-off potential of 4.2 V. However, as shown in **Fig. 6**, the discharge capacity degradation with an increase in cycle number at charge cut-off of 4.5 V was larger than that of 4.2 V.

Fig. 7 shows charge–discharge voltage curves of coin cells at 2nd and 50th cycles of LiCoO_2 electrodes with and without LiMgPO_4 powder. A horizontal axis (mA h g^{-1}) was shown by the bases of LiCoO_2 weight. LiCoO_2 electrodes with and without LiMgPO_4 exhibited similar polarization behavior at 2nd cycle. At 5th cycle, LiCoO_2 electrode caused larger polarization than that of LiCoO_2 electrodes with LiMgPO_4 . LiCoO_2 electrode with 2 wt.% LiMgPO_4 shows the highest charge–discharge capacities among the electrodes examined here. LiCoO_2 electrode with small amount addition of LiMgPO_4 might promote a lithium ion transport at the interface between electrode and electrolyte.

Fig. 8 shows discharge capacity degradation of LiCoO_2 electrodes with and without LiMgPO_4 . LiCoO_2 electrodes with LiMgPO_4 showed better cycle performance of LiCoO_2 electrodes. 2 wt. % LiMgPO_4 showed the best cycle performance. Oxidation products

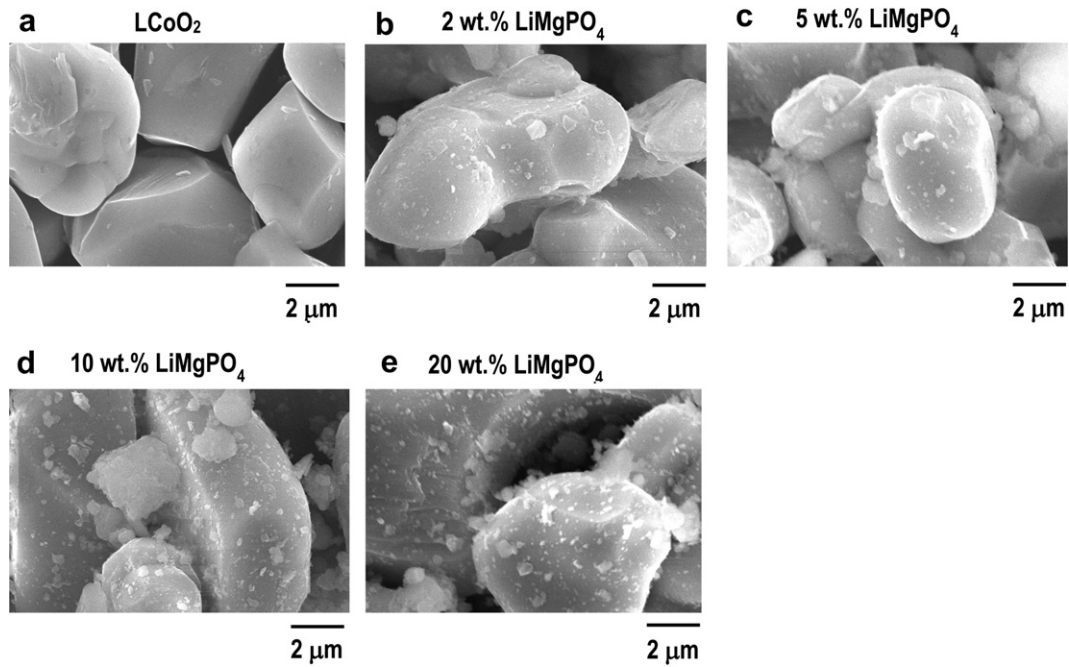


Fig. 3. SEM images of LiCoO₂ powder obtained by mixing mechanical milled LiMgPO₄ powder. a) LiCoO₂, b) 2 wt.% LiMgPO₄, c) 5 wt.% LiMgPO₄, d) 10 wt.% LiMgPO₄, d) 20 wt.% LiMgPO₄.

of electrolyte on LiCoO₂ with LiMgPO₄ might be chemically and electrochemically steady.

Fig. 9 shows Nyquist plots of ac impedance measurement results for Li/LiCoO₂ and Li/LiMgPO₄-modified LiCoO₂ cells after 2nd, 3rd, and 4th at cut-off potential of 4.5 V (vs. Li/Li⁺). Semicircles of low frequency region for Li/LiCoO₂ cells remarkably expanded

with an increase in cycle number. Such semicircle of low frequency region should be fitted to charge transport resistance (R_{ct}) at the interface of cathode/electrolyte [14,15]. Semicircles of low frequency region for Li/LiMgPO₄-modified LiCoO₂ cells did not expand with an increase in cycle number. These results mean that the electrode reactions smoothly proceed during charge–discharge

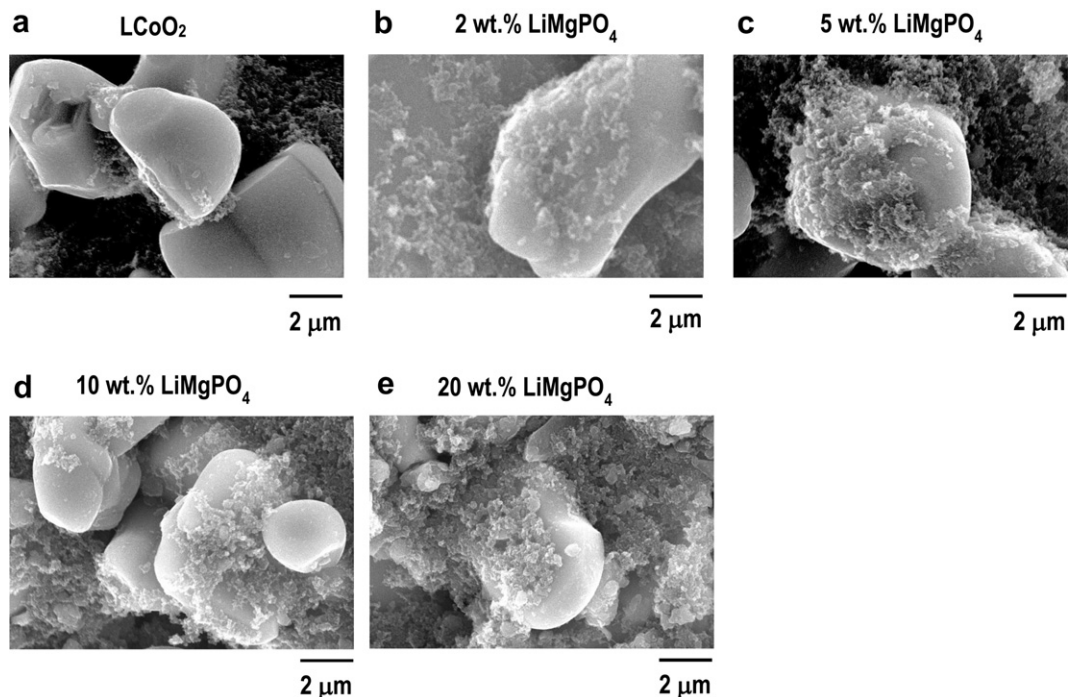


Fig. 4. SEM images of LiCoO₂ electrode surface with and without LiMgPO₄ powder. a) LiCoO₂, b) 2 wt.% LiMgPO₄, c) 5 wt.% LiMgPO₄, d) 10 wt.% LiMgPO₄, d) 20 wt.% LiMgPO₄.

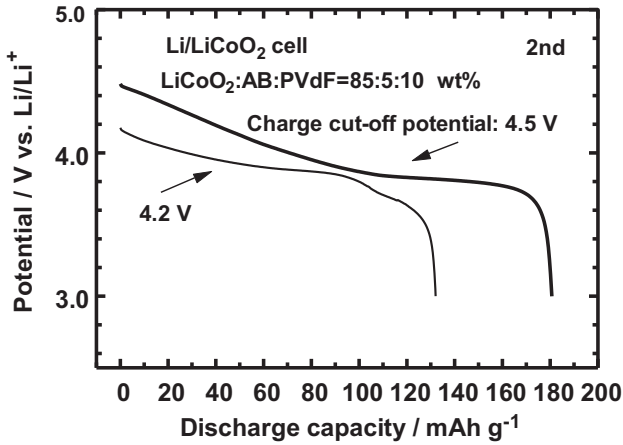


Fig. 5. Discharge curves of LiCoO₂ electrodes at 2nd cycle for charge cut-off potential of 4.2 and 4.5 V at constant current density of 0.5 mA cm⁻².

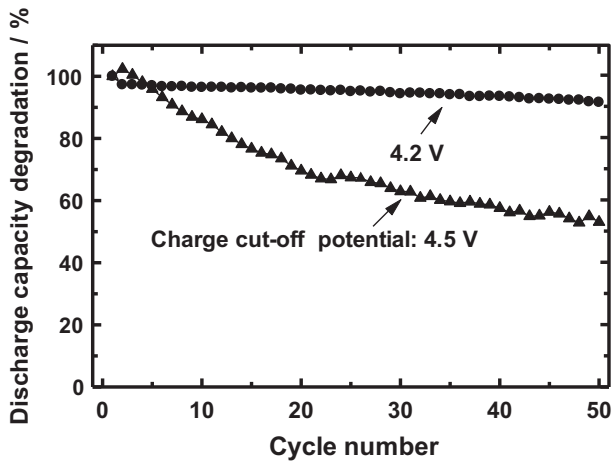


Fig. 6. Discharge capacity degradation of LiCoO₂ electrodes for charge cut-off potential of 4.2 and 4.5 V at constant current density of 0.2 mA cm⁻² during first cycle and 0.5 mA cm⁻² from 2nd to 50th cycle.

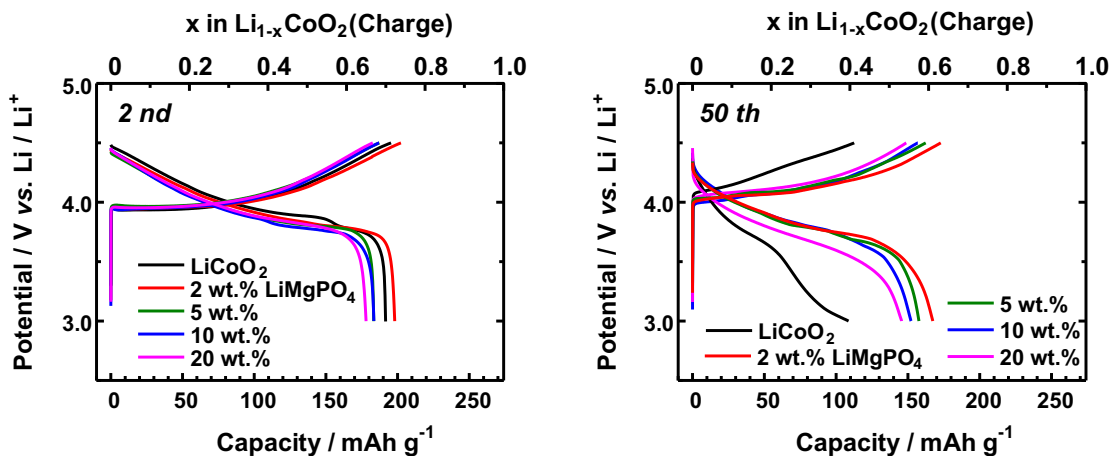


Fig. 7. Charge–discharge voltage curves of LiCoO₂ electrodes with and without LiMgPO₄ powder at 2nd and 50th cycle.

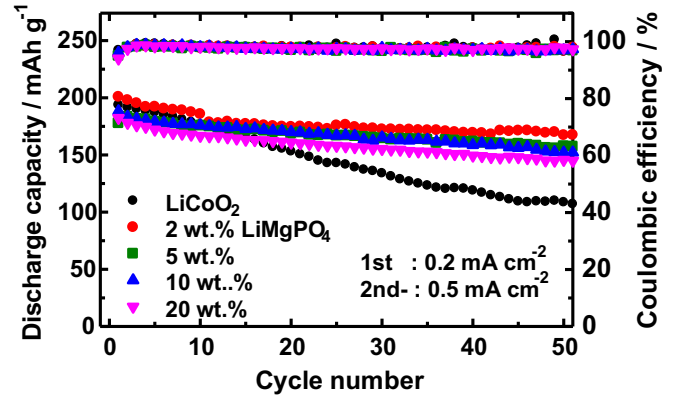


Fig. 8. Discharge capacity degradation of LiCoO₂ electrodes with and without LiMgPO₄ powder.

cycle for charging up to a high voltage of 4.5 V. The diameters of semicircles of low frequency region also tended to become large with an increase in LiMgPO₄ content. The increasing of LiMgPO₄ content is suggested to inhibit the lithium ion transport. It was found that there is the optimum coating amount of LiMgPO₄ on LiCoO₂.

Fig. 10 shows LSV curves of LiCoO₂ electrodes with and without LiMgPO₄, and LiMgPO₄ electrode from open-circuit potential to 8 V (vs. Li/Li⁺) for a scan speed of 0.5 mV s⁻¹. Oxidation currents were not detected for LiMgPO₄ electrode. The results mean that LiMgPO₄ has superior electrochemical stability and the oxidative decomposition of electrolyte dose not occur on LiMgPO₄ particles. LiCoO₂ electrode has oxidative peaks around 4.2 V and 6 V, respectively. The oxidative peaks around 4.2 V and 6 V correspond to the lithium extraction form LiCoO₂ and the oxidative decomposition of electrolyte on LiCoO₂ electrode, respectively. The oxidative peaks around 6 V of LiCoO₂ electrodes with LiMgPO₄ powder decreased and/or disappeared with increasing of the content of LiMgPO₄. Olivine-type structure LiMgPO₄ compound is highly electrochemically stable and poor electrically conductive, being due to the structure of PO₄ unit and transition metal free. LiMgPO₄ particles may inhibit the oxidative decomposition of electrolyte on the electrodes and dissolution phenomenon of Co⁴⁺ ion from LiCoO₂.

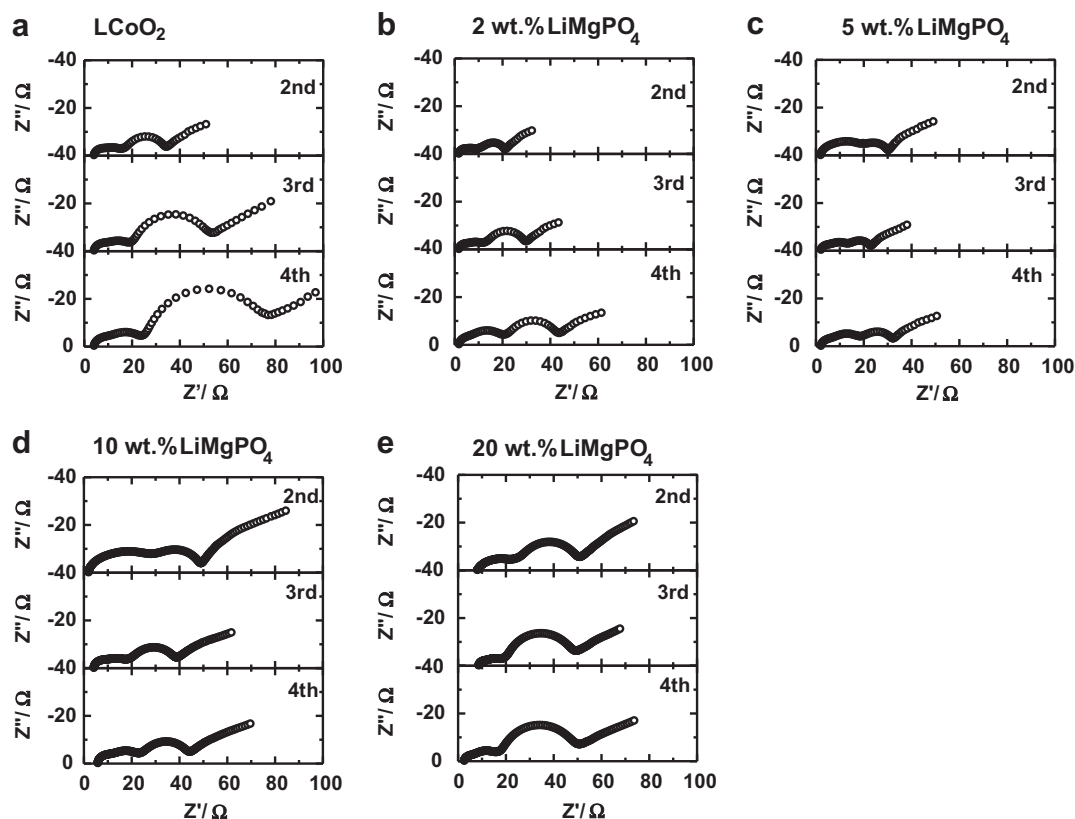


Fig. 9. Nyquist plots for Li/LiCoO₂ and Li/LiMgPO₄-modified LiCoO₂ cells after 2nd, 3rd, and 4th at cut-off potential of 4.5 V (vs. Li/Li⁺). a) LiCoO₂, b) 2 wt.% LiMgPO₄, c) 5 wt.% LiMgPO₄, d) 10 wt.% LiMgPO₄, e) 20 wt.% LiMgPO₄.

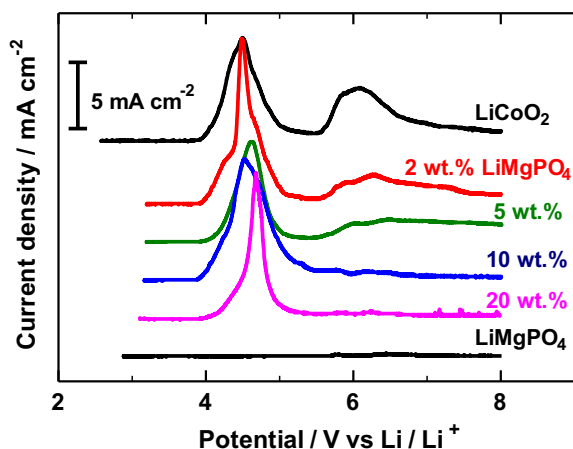


Fig. 10. LSV curves of LiCoO₂ electrodes with and without LiMgPO₄, and LiMgPO₄ electrode in the potential range from open-circuit potential to 8 V (vs. Li/Li⁺) for a scan speed of 0.5 mV s⁻¹.

4. Conclusions

Olivine-type LiMgPO₄-modified LiCoO₂ cathodes exhibited a good charge–discharge cycle performance for charge cut-off potential of 4.5 V (vs. Li/Li⁺) in lithium cells. LiMgPO₄ is one of promising coating material to enhance LiCoO₂ electrode properties for charge cut-off potential of 4.5 V LiMgPO₄ fine particle is

expected to work as a new buffer layer to inhibit decomposition of electrolytes on LiCoO₂ particle surface.

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