Kinetics of Li-ion transfer reaction at LiMn$_2$O$_4$, LiCoO$_2$, and LiFePO$_4$ cathodes

Agnieszka Swiderska-Mocek$^1$ · Andrzej Lewandowski$^1$

Abstract Kinetics of LiFePO$_4$, LiMn$_2$O$_4$, and LiCoO$_2$ cathodes operating in 1 M LiPF$_6$ solution in a mixture of ethylene carbonate and dimethyl carbonate was deduced from impedance spectra taken at different temperatures. The most striking difference of electrochemical impedance spectroscopy (EIS) curves is the impedance magnitude: tens of ohms in the case of LiFePO$_4$, hundreds of ohms for LiMn$_2$O$_4$, and thousands of ohms for LiCoO$_2$. Charge transfer resistances ($R_{ct}$) for lithiation/delitiation processes estimated from the deconvolution procedure were 6.0 Ω (LiFePO$_4$), 55.4 Ω (LiCoO$_2$), and 88.5 Ω (LiMn$_2$O$_4$), respectively. Exchange current density for all the three tested cathodes was found to be comparable ($0.55–1·10^{-2}$ mA cm$^{-2}$, $T=298$ K). Corresponding activation energies for the charge transfer process, $E^{\#}_{ct}$, differed considerably: 66.3, 48.9, and 17.0 kJ mol$^{-1}$ for LiMn$_2$O$_4$, LiCoO$_2$, and LiFePO$_4$, respectively. Consequently, temperature variation may have a substantial influence on exchange current densities ($j_0$) in the case of LiMn$_2$O$_4$ and LiCoO$_2$ cathodes.

Keywords LiMn$_2$O$_4$ · LiCoO$_2$ · LiFePO$_4$ cathodes · Graphite anode · Impedance · Kinetic parameters · Lithium-ion battery

Experimental

Materials

LiFePO$_4$ (carbon coated, battery grade, Aldrich), LiMn$_2$O$_4$ (Aldrich), LiCoO$_2$ (Aldrich), carbon black (CB, Fluka), poly(vinylidene fluoride) (PVdF, $M_W=180,000$ Fluka), lithium foil (Aldrich, 0.75 mm thick), and $N$-methyl-$2$-pyrrolidinone (NMP, Fluka) were used as received. LiPF$_6$ solution (1 M) in a mixture of ethylene carbonate and dimethyl carbonate (EC + DMC 1:1, Aldrich) was used as electrolyte.

Tested cathodes were prepared on golden current collectors by a casting technique from a slurry of electrode material, carbon black, and PVdF suspension in NMP. After solvent (NMP) evaporation at 120 °C in a vacuum, a layer of the electrode, containing the active material, the electronic conductor (CB), and a binder (PVdF) was formed.

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Procedures and measurements

Electrochemical properties of the cells were characterized using electrochemical impedance spectroscopy (EIS) and galvanostatic charging/discharging tests. The cycling measurements were taken with the use of the ATLAS 0461 MBI multichannel electrochemical system (Atlas-Sollich, Poland). Impedance spectroscopy measurements were performed using the Gamry 1000 multichannel electrochemical system (USA) at different temperatures. Tested anodes were separated from metal-lithium counter and reference electrode by the glass microfiber GF/A separator (Whatmann, 0.4–0.6-mm thick), all placed in an adopted Swagelok® connecting tube. Typically, the mass of the lithium was ca. 31 mg (0.785 cm²), while that of cathodes was 3.0–4.0 mg. The cells were assembled in a glove box in the dry argon atmosphere. After electrochemical measurements, the cells were disassembled and the cathodes were washed with DMC and dried in vacuum at room temperature. The morphology of electrodes was observed with a scanning electron microscope (SEM, Tescan Vega 5153). The BET surface of pristine electrode materials was determined with an Autosorb iQ apparatus (Quantochrome Instruments, UK) and particle size distribution with a Zetasizer Nano ZS (Malvern Instruments Ltd., UK).

Results and discussion

BET surface, size distribution, and SEM images

Specific surface area of cathode materials from BET analysis was between 15.4 and 2.05 m² g⁻¹ (Table 1). Particle size distribution is shown in Fig. 1. LiFePO₄ and LiCoO₂
Materials contained particles of diameters between 1 and 4 μm, with the maximum amount of ca. 2 μm. The size distribution of LiMn$_2$O$_4$ particles was broader (2 and 7 μm with a maximum at 4–6 μm). Figures 2, 3, and 4 show SEM images of cathodes (1) after electrode formation but before its cycling and (2) in the discharged state after the second cycle. In the case of all cathodes, their cycling results in the formation of small particles. In the case of LiFePO$_4$ and LiMn$_2$O$_4$, the diameter of particles remained similar while LiCoO$_2$ was converted into material of a smaller diameter.

**Impedance and kinetic parameters**

Figure 5 shows impedance spectra of tested cathode materials at room temperature. All curves consist of two semicircles at the high frequency region and a straight line at low frequencies (in the case of LiFePO$_4$, only a part of the first semicircle can be seen). The most striking difference is the impedance (resistance) magnitude: tens of ohm in the case of LiFePO$_4$, hundreds of ohm for LiMn$_2$O$_4$, and thousands of ohm for LiCoO$_2$. Impedance spectra were deconvoluted according to the equivalent circuit shown in Fig. 6. It was selected from a
library of circuits based on two time constants due to best correlation of fits with experimental data. Passivation film ($R_f$) and charge transfer ($R_{ct}$) resistances obtained from the deconvolution procedure are shown in Table 1. Both $R_f$ and $R_{ct}$ given in ohms are expressed versus the geometrical surface area of electrodes (1.27 cm$^2$). It can be seen from Table 1 that resistance of the passivation film differs by two orders of magnitude depending on the electrode material: it was 4.9 $\Omega$ for LiFePO$_4$, ca. 20 times more for LiMn$_2$O$_4$ (102 $\Omega$), and as high as 645 $\Omega$ for LiCoO$_2$. Charge transfer resistances ($R_{ct}$) estimated from the deconvolution procedure were between 6.0 and 88.5 $\Omega$ (Table 1). Those resistances can be expressed against the anode real surface area $A$ (estimated from BET measurements $S = m S_{BET}$) as $R_{ct} S$ (expressed in $\Omega$cm$^2$).

Charge transfer resistances may be converted into surface area independent of exchange current densities:

$$j_0 = \frac{RT}{FS R_{ct}}$$

(1)

Both $R_{ct} S$ and $j_0$ values are given in Table 1. It can be seen that while charge transfer resistances differ for one order of
magnitude, the corresponding $R_{ct}S$ values are comparable: from ca. 4.7 to ca. 2.5 $\text{k}\Omega\text{cm}^2$. Consequently, exchange current density for all the three cathode materials is also comparable, amounting to $10^{-2}$ mAm$^{-2}$: from ca. 0.55 $10^{-2}$ mAm$^{-2}$ ($\text{LiMn}_2\text{O}_4$) to ca. 0.94 $10^{-2}$–1.01 $10^{-2}$ mAm$^{-2}$ ($\text{LiCoO}_2$ and $\text{LiFePO}_4$). Exchange current densities can be found in the literature for the $\text{LiFePO}_4$ material $[16–18]$. In general, $j_o$ values are reported in a broad range between $10^{-5}$ mAm$^{-2}$ ($5.1910^{-3}$ mAm$^{-2}$ $[17]$, 2.12 $10^{-5}$ mAm$^{-2}$ $[18]$), and $10^{-1}$ mAm$^{-2}$ ($1.710^{-1}$ mAm$^{-2}$ $[16]$). However, a comparison of the present results with literature data is difficult because (i) different solvents or electrolytes were used and (ii) the real surface areas of electrodes were not reported or even not taken into account in calculations. For the other cathodes ($\text{LiCoO}_2$ and $\text{LiMn}_2\text{O}_4$), $R_{ct}S$ and $j_o$ values are not available.

Kinetic parameters of cathodes may be compared to the corresponding data for the metallic lithium $[9, 25–30]$ anode. A typical reported value is of the order of $10–10^{-1}$ mA cm$^{-2}$, depending on the solvent, electrolyte, and its concentration $[30]$. Exchange current density values, expressed versus the active material specific surface, suggest that the kinetics of the charge transfer taking place at the cathode is slower in
comparison to metallic lithium, while the surface area is larger. To our knowledge, available literature does not present exchange current densities for LiC$_6$ (graphite) anodes working together with classical LiPF$_6$ electrolytes. Generally, $R_{ct}$ values determined from impedance spectroscopy for a lithiated graphite anode can be found in the literature; however, resistance depends on the electrode size (real surface area), which usually is not mentioned. Therefore, the $j_0$ value for LiC$_6$ was measured in the present study in the same way as for cathodes (the impedance spectrum for the LiC$_6$ anode is shown in Fig. 7) and data are listed in Table 1. It can be seen that the exchange current density is comparable to that characteristic of anodes ($0.77 \cdot 10^{-2}$ mA cm$^{-2}$).

Values of $R_f$ and $R_{ct}$ measured at different temperatures and plotted as $-\ln R = f(T^{-1})$ provide electrode size-independent charge transfer activation energy $E^\theta_{ct}$. Figure 8 shows the Arrhenius plot for a LiFePO$_4$ cathode as an example. Both $E_f^\theta$ and $E^\theta_{ct}$ values for all cathodes are shown in Table 1. It can be seen that activation energies for the Li$^+$ ion conduction in passivation film and charge transfer reaction are similar in the case of LiMn$_2$O$_4$ and LiCoO$_2$ while in the case of the LiFePO$_4$ cathode, both $E_f^\theta$ and $E^\theta_{ct}$ are considerably lower. Activation energies for the charge transfer process taking places at cathodes can be found in the literature [11–15]. Again, a comparison of data is difficult due to different solvents, electrolytes, and their concentrations. Some data are reported for polymer electrolytes. In addition, the state of cathodes intercalation is different, which is equivalent to a
comparison of different compounds. For example, the $E_{ct}^#$ value found here for the LiCoO$_2$/1 M LiPF$_6$ in EC + DMC system is 48.9 kJmol$^{-1}$, comparable to that reported for the LiCoO$_2$/1 M LiClO$_4$ or LiCF$_3$SO$_3$ in PC (46–48 kJmol$^{-1}$ [14]). Both values were measured at a potential of ca. 3.9 V versus metallic lithium. The corresponding activation energy measured at a higher potential (4.2 V), equivalent to a lower degree of intercalation, was reported to be much lower (ca. 25 kJmol$^{-1}$ [15]).

Compatibility of cathodes with the LiC$_6$ anode

Li-ion batteries typically contain a carbon anode, which capacity (for graphite ca. 370 mAh g$^{-1}$) is usually higher in comparison to that characteristic of cathodes (Table 2). However, the capacity of the CF$_x$ material is very high (ca. 900 mAh g$^{-1}$), and hence, literature kinetic data for this cathode [31] are also shown in Table 2. The ratio of the cathode and graphite mass should be equal to the corresponding ratio of specific capacity ($n_c/n_G = q_c/q_G$) to maximize active material utilization. The ratio $m_c/m_G$ indicates also the mass of the cathode compatible with 1 g of carbon material. It can be seen from Table 2 that the mass ratio $n_c/n_G$ for LiMn$_2$O$_4$, LiCoO$_2$, and LiFePO$_4$ cathodes is between 3.08 and 2.18 in contrast to the CF$_x$ material ($n_{CF}/n_G = 0.41$). On the other hand, from the point of view of power, the ratio of anodic and cathodic charge transfer resistance should be close to 1 (a more resistive electrode determines the operation rate). The ratio of cathodic and anodic resistances $R_c/R_G$ can be calculated from the ratio of electrode surface $S_c/S_G$ and exchange current densities $f_c/f_G$:

$$\frac{R_c}{R_G} = \frac{S_G}{S_c} f_G$$

(2)

The $R_c/R_G$ ratio values shown in Table 2 fall within a broad range between 0.13 and 10.04. While LiMn$_2$O$_4$ and LiCoO$_2$ cathodes ($R_c/R_G \approx 1$) are kinetically compatible with the carbon anode, the situation in the case of other cathodes is different. The LiFePO$_4$ material shows resistance by one order of magnitude lower than the equivalent amount of carbon. In contrast, the CF$_x$ cathode is characterized by resistance by one order of magnitude higher than the equivalent amount of the anode.

Conclusions

The most striking difference of EIS curves is the impedance magnitude: tens of ohms in the case of LiFePO$_4$, hundreds of ohms for LiMn$_2$O$_4$, and thousands of ohms for LiCoO$_2$. Charge transfer resistances ($R_{ct}$) for the lithiation/delitiation process estimated from the deconvolution procedure were 6.0 $\Omega$ (LiFePO$_4$), 55.4 $\Omega$ (LiCoO$_2$), and 88.5 $\Omega$ (LiMn$_2$O$_4$). Exchange current density for all the three tested cathodes was found to be comparable ($0.55 \cdot 10^{-2} – 1 \cdot 10^{-2}$ mA cm$^{-2}$, $T = 298$ K).

Corresponding activation energies for the charge transfer process, $E_{ct}^#$, differed considerably: 66.3, 48.9, and 17.0 kJmol$^{-1}$ for LiMn$_2$O$_4$, LiCoO$_2$, and LiFePO$_4$, respectively.

### Table 2  Calculated compatibility parameters of graphite anode (G) and cathodes (c): theoretical capacity $q$, mass $n$ of cathode material compatible with 1 g of graphite ($n_c = 1$ g$/q_c/q_G$), real surface area of electrode material $S$ (calculated as $nS_{BET}$), ratio of graphite and cathode real surface ($S_G/S_c$), exchange current density ($f_c/f_G$), and charge transfer resistance ($R_c/R_G$)

|        | LiMn$_2$O$_4$ | LiCoO$_2$ | LiFePO$_4$ | CF$_x$ [25] | G |
|--------|---------------|------------|------------|-------------|---|
| $q$ (mAh g$^{-1}$) | 120 | 140 | 170 | 900 | 370 |
| $n$ (g) | 3.08 | 2.64 | 2.18 | 0.41 | 1.00 |
| $S$ (cm$^2$) | $7.08 \cdot 10^4$ | $5.41 \cdot 10^4$ | $3.36 \cdot 10^5$ | $3.84 \cdot 10^5$ | $6.00 \cdot 10^4$ |
| $S_G/S_c$ | 0.85 | 1.11 | 0.18 | 0.16 | – |
| $f_c/f_G$ | 1.31 | 0.77 | 0.71 | 64.29 | – |
| $R_c/R_G$ | 1.11 | 0.85 | 0.13 | 10.04 | – |
respectively. Consequently, temperature variation may have a substantial effect on $j_o$ in the case of $\text{LiMn}_2\text{O}_4$ and $\text{LiCoO}_2$ cathodes.

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