—Communication—

Protection against H₂O Impurity for Cyclability of Lithium Anode in Propylene Carbonate Electrolyte by an Existence of CO₂

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Introduction

A rechargeable lithium battery has high energy density and high power. However, the battery has the problem that the cycle life of the lithium anode is shortened by the lithium dendritic deposition and the side reaction between the electrolyte solution and the anode. It is known that the life is influenced by several additives or impurities in the electrolyte solutions^{1,2)}. The influence of CO₂ in an electrolyte was reported previously³⁾. In this communication, we report the enhancement of cyclability due to CO₂ existence in propylene carbonate (PC) electrolyte under even much amount of H₂O impurity by using ac impedance measurement during galvanostatic charging and discharging^{4,5)}.

Experimental

Reagent grade PC solvent with 1.0 mol dm⁻³ LiClO₄ was used as electrolyte solution. The supporting electrolyte had a water content less than 20 ppm. CO₂ of 99.99 % purity includes a water content less than 20.3 ppm. The CO₂ gas was bubbled into the PC electrolyte for 30 minutes before the electrodeposition of the lithium to investigate the influence of CO₂. Distilled H₂O was added 3000 ppm in the PC electrolyte to investigate the influence of H₂O. The lithium deposited on nickel substrate and Li/Li⁺ was used as a working and a reference electrode, respectively. The cyclability of galvanostatic charging and discharging was determined by the procedure proposed by Koch et al.,⁶⁾ that is, the lithium deposited at 1 mA cm⁻² and 1 C cm⁻² was dissolved and deposited at 0.2 C cm⁻²

and the same current density. During the cycle of charging and discharging, the *in-situ* ac impedance measurement already reported by us⁴⁾ was carried out using a galvanostat and a frequency response analyzer (NF Electric Instruments FRA S-5720C) with a frequency range of 10 Hz to 20 kHz. The ac current of 10 μA was applied to the electrochemical cell with dc current. All measurements were performed under a dry argon gas atmosphere.

Results and Discussion

Figure 1 shows Cole-Cole plots obtained by the *in-situ* impedance measurement during charging at 1 mA cm⁻² in the PC electrolyte with and without CO₂. The results are measured during the charging of the first cycle at 0.2 C cm⁻² after the lithium is electrodeposited on nickel substrate at 1 C cm⁻². The impedance spectra display semi-circle in higher frequency region. The charge transfer resistance (R_{ct}) due to lithium deposition is estimated from the diameter of the semi-circle according to the usual method⁷⁾. Since the diameter is nearly equal to the R_{ct} value measured by potentiostatic *ex-situ* measurement at open circuit potential, the diameter by the *in-situ* measurement is able to be estimated as the R_{ct} value by the *ex-situ* measurement⁴⁾.

In Fig.1, the R_{ct} value in the electrolyte with CO₂ is smaller than that without CO₂. Thus, the coexistence

Fig.1 *In-situ* impedance spectra of electrodeposited lithium in PC solutions with and without CO₂ during charging at 1 mA cm⁻².

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of CO_2 makes the charge transfer reaction fast or smooth.

Figure 2 shows the R_{ct} value estimated by *in-situ* measurement for each cycle of charging and discharging in the electrolyte with and without CO_2 . Both charging and discharging, the R_{ct} value without CO_2 begins to increase sharply near the cycles when the life in the anode approaches to the end, that is, the discharge potential reaches at 1 V vs. Li/Li^+ . In the electrolyte with CO_2 , the R_{ct} increase is less sharp than that without CO_2 and the cycle number becomes twice as compared with that without CO_2 . This result was also obtained in the case of the charging and discharging without CO_2 after the lithium was electrodeposited with CO_2 on the nickel substrate. The coexistence of CO_2 clearly makes the cyclability of the anode better than that in the electrolyte without CO_2 .

To investigate whether the enhancement of the charging and discharging of lithium anode by CO_2 is effective in the much harder conditions containing H_2O in the electrolyte, the *in-situ* measurement was done during charging and discharging in the electrolyte with added 3000 ppm H_2O without CO_2 after the lithium was electrodeposited with CO_2 without added H_2O on the nickel substrate. Figure 3 shows the variation of the R_{ct} value obtained by the above process during charging and discharging as a function of cycle number. The R_{ct} value during charging and discharging with added H_2O without CO_2 after the electrodeposition without CO_2 and added H_2O on the substrate is also shown in Fig.3 for the reference.

In the case of the electrodeposition without CO_2 , the cycle life in the electrolyte with H_2O is much shorter than that in the case without H_2O . On the other hand, in the case of the deposition with CO_2 the cycle number makes surprisingly longer. The cyclability is almost the same with that in the case of the CO_2 coexistence without added H_2O during the deposition on the nickel substrate and the cycle of charging and discharging, even though the R_{ct} values become relatively larger with the cycle. Thus, even at the conditions of 3000 ppm H_2O coexistence the enhancement effect of cyclability by CO_2 is confirmed.

Conclusion

The coexistence of CO_2 in the PC electrolyte makes the cycle life of the lithium anode longer than the life in the electrolyte without CO_2 . Although 3000 ppm H_2O exists in the PC electrolyte, the enhancement effect of CO_2 is remarkably confirmed to be appeared and the protection against amount of H_2O impurity by CO_2 is recognized.

References

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Fig.2 Variations of charge transfer resistance (R_{ct}) with cycle number during charging and discharging at 1 mA cm^{-2} in PC solutions with and without CO_2 .

Fig.3 Variations of charge transfer resistance (R_{ct}) with cycle number during charging and discharging at 1 mA cm^{-2} in PC solution with 3000 ppm H_2O . The lithium is electrodeposited in PC solutions with and without CO_2 at the same current density before charging and discharging.