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Effects of Various Electrolytes on the Electrochemical Performance of Spinel $LiMn_2O_4$ in Aqueous Solutions

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The effects of various electrolytes on the electrochemical performance of $LiMn_2O_4$ electrodes are investigated. It is shown that for an increased Li^+-ion concentration, the potential of $LiMn_2O_4$ electrodes is shifted to a positive value, improving the kinetics. Anions in electrolytes exert a strong influence on the electrochemical performance of $LiMn_2O_4$ electrodes, which results from Mn dissolution and oxygen evolution. The electrode in a 5 M $LiNO_3$ solution with minimal Mn dissolution and a high oxygen overpotential exhibited good rate capability and cyclability. Conversely, in a LiCl solution, the extent of Mn dissolution is large, and the electrode is affected simultaneously by O_2 and Cl_2 evolution. Although the addition of zinc salts inhibits certain side reactions, a sharp deterioration in the capacity results during charge/discharge cycling. The addition of zinc salts into the Li_2SO_4 solution also results in an increase in the amount of dissolved Mn. However, the oxygen evolution is markedly attenuated, and the capacity retention rate of the $LiMn_2O_4$ electrode in the sulfate solution is significantly improved, increasing from 35 to 58% after 1000 cycles at 2 C.

Keywords: Spinel $LiMn_2O_4$, aqueous electrolyte, Mn dissolution, capacity fade, mechanism

1. INTRODUCTION

Spinel $LiMn_2O_4$ has the following advantages: natural abundance, low cost, low toxicity and simple preparation, and it exhibits good kinetics for the lithium insertion/extraction reaction and a relatively high potential. It became the most attractive cathode materials for aqueous lithium ion batteries. However, as in organic electrolytes, during the charge and discharge process, it is easy to occur Jahn-Teller effect, manganese dissolution and structural distortion and other phenomena [1], which made capacity fading relatively serious (especially at low current rates and relatively high temperature) [2-3]. So far, surface coating of metal oxides[4-6] on $LiMn_2O_4$ or doping some other transition elements (or ion) [7-9] during the synthesis process of $LiMn_2O_4$ are the main ways to improve the cycle stability. Additionally, it has been reported that the electrochemical performance of $LiMn_2O_4$ electrodes is closely associated with the nature of the electrolyte solution, especially the type of anions [10]. Until now, for aqueous lithium-ion batteries, different aqueous electrolytes have been used, such as $LiNO_3$ [11-13], Li_2SO_4 [14-16], $LiCF_3SO_3$ [17], etc. Among these electrolytes, $LiNO_3$ and Li_2SO_4 solutions are the most frequently used electrolytes. Yet, the effect of the electrolyte mechanism on the capacity fading of spinel $LiMn_2O_4$ is ambiguous.

Compared with that of the cathode material, $LiMn_2O_4$, the instability of the discharged anode materials in water, especially in the presence of oxygen, is more serious [18]. Therefore, Wang [15] et al. proposed a new hybrid electrochemical super capacitor in which activated carbon was used as the negative electrode and the lithium-ion intercalation compound $LiMn_2O_4$ as the positive electrode in a Li_2SO_4 aqueous electrolyte. The cell exhibits excellent cycling performance. But, it only delivers a specific energy of ca. 35 W h/kg based on the weight of the active electrode materials. In 2012, Yan et al. [19] reported a new $LiMn_2O_4/ZnCl_2+LiCl/Zn$ rechargeable hybrid aqueous batteries. The battery operates via redox intercalation/de-intercalation at the cathode and metal ion deposition/dissolution at the anode. The battery operates at approximately 2 V, and preliminarily tests show excellent cycling performance. It was estimated that this battery can provide approximately 50-80 Wh kg^{-1} of practical energy density. Thus, it is necessary to investigate the effect of Zn^{2+} ions on the electrochemical performance of $LiMn_2O_4$ electrodes.

In previous reports, researches focus on the electrochemical properties of $LiMn_2O_4$ in Li_2SO_4 and $LiNO_3$ electrolytes. However, pure Li_2SO_4 and $LiNO_3$ solutions are neutral. In this paper, we added $ZnSO_4$ into Li_2SO_4 electrolyte, by which the pH value can change to nearly 4. In such weak acidic electrolyte, the overpotential of oxygen evolution on substrate is increased, which can further improve the cycling stability. We also studied the electrochemical properties of the $LiMn_2O_4$ electrode in various aqueous electrolytes, including Li_2SO_4, $LiNO_3$ and LiCl solutions, was investigated with an emphasis on the rate capability and full charge/discharge cycling. Based on this, the effect of the mechanism of the aqueous electrolytes on the electrochemical performance of the $LiMn_2O_4$ electrode is elucidated.

2. EXPERIMENTAL

$LiMn_2O_4$ electrodes were fabricated as follows: the $LiMn_2O_4$ particles with an average particle size of 12.8 μm (purchased from Yunnan Yuxi Huilong Technology Co. Ltd.) were mixed with 10 wt% carbon black and 5 wt% PTFE binder to form a homogeneous slurry. Then, the blended slurries were pressed onto a titanium mesh current collector with an apparent area of 1×1 cm^2, followed by drying at 120 °C for 5 h.

Electrochemical properties of the $LiMn_2O_4$ electrodes were evaluated in a three-electrode cell, with $LiMn_2O_4$ as the working electrodes and activated carbon as counter electrodes, and saturate calomel electrode (SCE, 0.242 V vs normalhydrogen electrode) was used as the reference electrode. Aqueous solutions of 1 M Li_2SO_4, 2 M Li_2SO_4, 1 M Li_2SO_4 + 2 M $ZnSO_4$, 2 M Li_2SO_4 + 2 M Li_2SO_4, 5 M $LiNO_3$, 4 M LiCl and 3 M LiCl + 4 M $ZnCl_2$ with pH values of 6.33, 6.71, 4.56, 4.65, 7.37, 8.58 and 3.08, respectively, were used as the electrolytes. Cyclic voltammetry and ac impedance tests were performed using a Solartron instrument, Model 1280Z. The impedance spectra were measured at a given potential of 0.6 V vs. SCE for the electrodes in the 1 M Li_2SO_4, 1 M Li_2SO_4 + 2 M $ZnSO_4$, 2 M Li_2SO_4 + 2 M $ZnSO_4$ and 5 M $LiNO_3$ solutions, respectively. Galvanostatic charge/discharge experiments were conducted between 0.2 and 1.2 V using a LAND CT2001A autocycler (China). All tests were conducted at 25 °C.

A total amount of 110 mg of the $LiMn_2O_4$ electrodes were soaked in 1 M Li_2SO_4, 2 M Li_2SO_4, 1 M Li_2SO_4 + 2 M $ZnSO_4$, 4 M $LiNO_3$, 5 M $LiNO_3$, 6 M $LiNO_3$ and 3 M LiCl + 4 M $ZnCl_2$ solutions (10 mL), respectively, and the containers were kept in an thermostat oven at 25 °C for two weeks. Inductively coupled plasma atomic emission spectroscopy (SPECTRO ARCOS EOP) was used for the quantitative analyses of Mn in the solutions.

3. RESULTS AND DISCUSSION

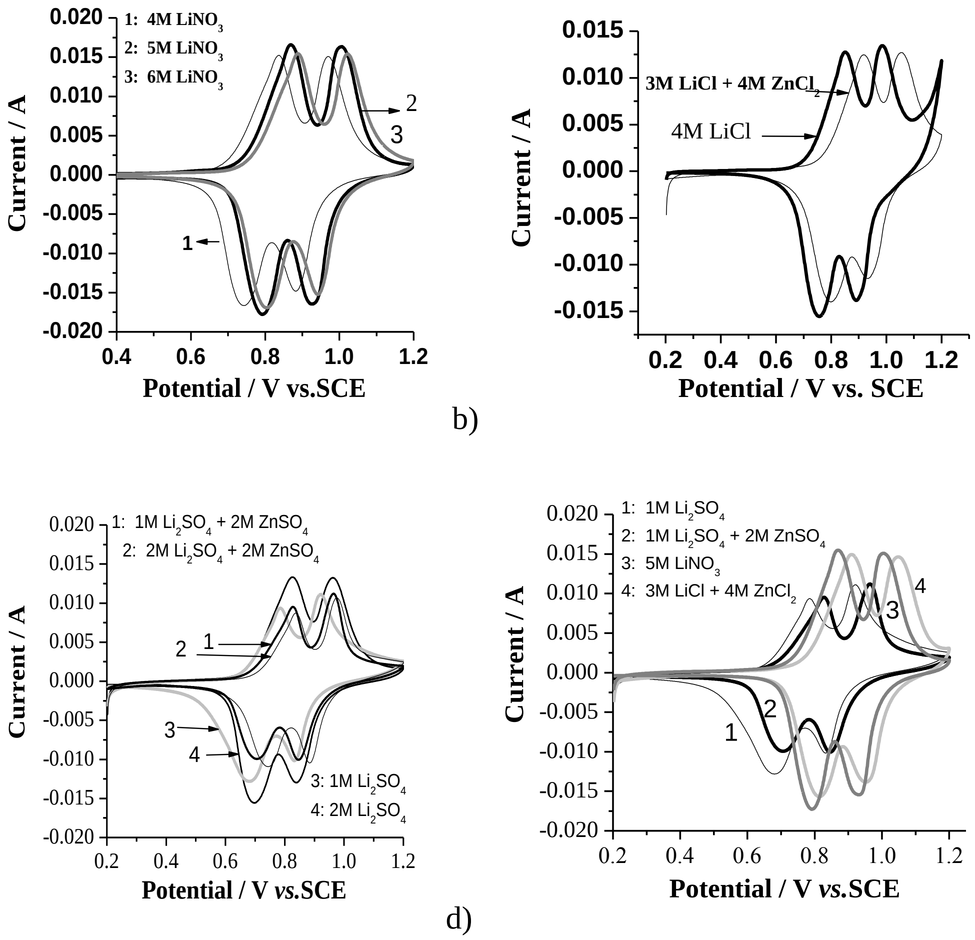


Figure 1. Cyclic voltammogram profile of the $LiMn_2O_4$ electrode in different aqueous solutions containing anions of NO_3^-(a), Cl^-(b), SO_4^{2-}(c) and three types(d) , scanning rate: $1 mVs^{-1}$.

Fig. 1 shows the cyclic voltammograms (1st cycle) of the $LiMn_2O_4$ electrode in the various aqueous solutions at 1 mVs^{-1}. Two distinguishable couples of reversible redox peaks can be observed, which is consistent with the reports in the literature [1-3]. In addition to the active species, the Li^+ cation, anions in the electrolytes greatly influence the electrochemical behavior of the $LiMn_2O_4$ electrodes. As shown in Fig. 1a, with increased Li-ion concentration in the $LiNO_3$ solutions, the peak potential shifts to a positive value, and the redox currents increase. When the Li^+-ion concentration is 5 M, the smallest peak separation and highest peak current response are obtained, suggesting the best kinetics. In the 4 M LiCl solution, as shown in Fig. 1b, significant gas evolution is observed. This results not only from oxygen evolution but also from chlorine evolution. The addition of $ZnCl_2$ into 4 M LiCl solution markedly suppresses the side reactions of oxygen and chlorine evolution. Additionally, the peak potentials of anode and cathode are shifted to the positive direction. However, the peak-current response decreases. In solutions containing SO_4^{2-}, as shown in Fig. 1c, the addition of $ZnSO_4$ leads to a reduction in the peak current, possibly owing to the decrease in the ion conductivity. In contrast, as shown in Fig. 1d, the peak potential of the $LiMn_2O_4$ electrodes is the highest in solutions containing Cl^- ions. As a result, the effect of O_2 and Cl_2 evolution is relatively serious. In the aqueous solutions containing SO_4^{2-}, the redox current is considerably lower than that in the solutions containing NO_3^- and Cl^-. However, the anode and cathode peak potentials shift to the negative direction. This suggests that the influence of the oxygen evolution is attenuated. These results show that the reversibility of the electrode reaction in the 5 M $LiNO_3$ solution is far superior to that in the Li_2SO_4 solutions. Additionally, the side reaction of gas evolution is relatively serious in the LiCl solutions. As seen by the peak-potential separation and the peak-current response, $LiNO_3$ solutions with relatively high concentrations are electrochemically favorable for the $LiMn_2O_4$ electrode.

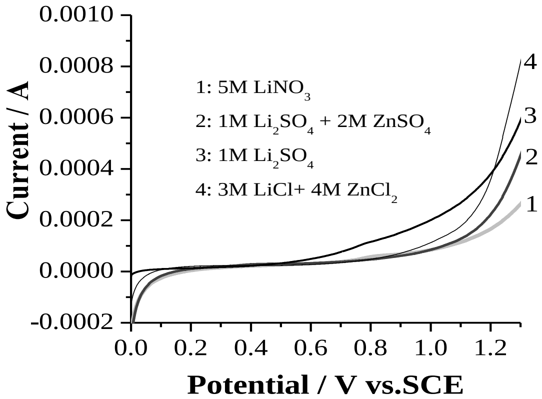


Figure 2. Effect of electrolyte on oxygen evolution reaction on a titanium mesh electrode, scan rate: 10mV s^{-1}.

The need to suppress O_2 formation is critical for $LiMn_2O_4$ electrodes used in aqueous media. The rate of the oxygen evolution reaction (OER) depends greatly on the overpotential of oxygen on the current-collector electrode. It is expected that this overpotential is closely associated with the electrolyte. Anodic polarization curves at 10 mV s^{-1} on a titanium-mesh electrode in various electrolytes are shown in Fig. 2. It is found that in 1 M Li_2SO_4 solution, the oxygen evolution occurs early at 0.6 V (vs. SCE), indicative of a rather low oxygen overpotential. In contrast, in a solution contain Cl^- ions, with the shift of potentials to the positive direction, the corresponding current increases dramatically. This may be attributed to the simultaneous occurrence of oxygen and chlorine evolution. The addition of $ZnSO_4$ into the 1 M Li_2SO_4 solution effectively inhibits oxygen evolution, which is attributed to the decrease in the pH value. However, the current for O_2 evolution is still higher than that in the $LiNO_3$ solution, especially when the potential is higher than 1.2 V vs. SCE.

Table 1. Mn dissolution of the storage of $LiMn_2O_4$ electrode in different electrolytes for 2 weeks

Electrolyte	Li_2SO_4		$LiNO_3$			1M Li_2SO_4+ 2M $ZnSO_4$	1M LiCl+ 2M $ZnCl_2$
	1M	2M	4M	5M	6M		
Mn/ppm	0.94	1.79	0.05	0.06	0.04	3.72	2.59

The spinel $LiMn_2O_4$ was stored in 10 mL each of the various electrolytes for two weeks. The results are summarized in Table 1. The amount of dissolved Mn from $LiMn_2O_4$ in the $LiNO_3$ solutions is the lowest, and it remains nearly constant with changes in the $LiNO_3$ concentration. Conversely, in Li_2SO_4 solutions, with increased Li_2SO_4 concentration, the amount of dissolved Mn from $LiMn_2O_4$ rises proportionally. The addition of $ZnSO_4$ or $ZnCl_2$ further increases the amount of dissolved Mn from $LiMn_2O_4$ because the pH value of the solution is decreased to approximately 4.5. Thus, for Mn dissolution, the anions in the aqueous solutions and the pH value of the solutions play a critical role.

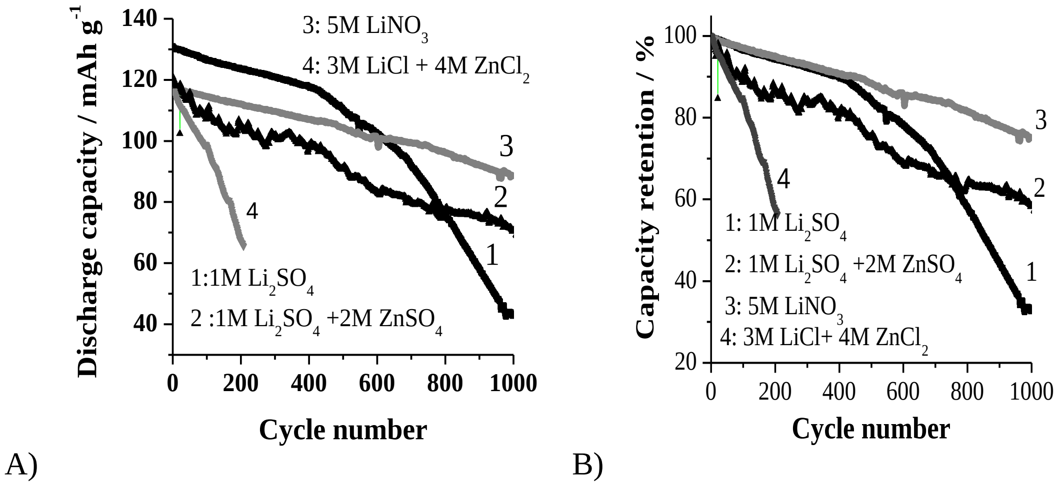


Figure 3. Change of discharge capacity (A) and capacity retention of $LiMn_2O_4$ electrode with cycling number in various electrolytes at a current rate of 2C.

Fig. 3 reveals the cycling performance of the $LiMn_2O_4$ electrodes in the various electrolytes at a current rate of 2 C. In different solutions containing Li^+ ions with concentrations above 3 M, the initial discharge capacity reaches 120-130 mAh g^{-1} but shows different fading magnitudes. In terms of long charge/discharge cycling performance, the $LiMn_2O_4$ electrode in the 5 M $LiNO_3$ solution exhibits the best cycling stability with a capacity retention of 75% after 1000 cycles. In the 1 M Li_2SO_4 and 5 M $LiNO_3$ solutions, the curves of the capacity vs. cycling number for the $LiMn_2O_4$ electrode are almost overlapped in the initial 400 cycles. However, after 400 cycles, the fading magnitudes begin different. The electrode in the 1 M Li_2SO_4 solution presents dramatic deterioration with a capacity retention of only 32% after 1000 cycles. After the addition of $ZnSO_4$ into the 1 M Li_2SO_4 solution, the cycling stability of the $LiMn_2O_4$ electrode is significantly improved with a capacity retention of 58% over 1000 cycles. However, in the 3 M LiCl + 4 M $ZnCl_2$ solution, a sharp decrease in the discharge capacity is observed with cycling number. After only 200 cycles, the discharge capacity of the electrode decreases to 70 mAh g^{-1} with a capacity retention of only 56%.

As can be seen, the cycling stability of the $LiMn_2O_4$ electrode in aqueous media is directly dependent on the degree of oxygen evolution and Mn dissolution. In $LiNO_3$ solutions, the good cycling stability of the $LiMn_2O_4$ electrode is ascribed to the high overpotential of the OER and the small amount of dissolved Mn. In the 1 M Li_2SO_4 solution, the rate of OER and the amount of dissolved Mn increase significantly. A substantial decrease in the discharge capacity of the $LiMn_2O_4$ electrode is observed during prolonged charge/discharge cycling. Although the addition of $ZnSO_4$ into the 1 M Li_2SO_4 solution increases the amount of dissolved Mn, the cycling stability of the $LiMn_2O_4$ electrode is improved considerably due to a pronounced increase in the overpotential of oxygen evolution. In a chlorine-salt solution, the amount of dissolved Mn from the $LiMn_2O_4$ is relatively high. The electrode reaction of $LiMn_2O_4$ is affected by the simultaneous side reactions of oxygen and chlorine evolution. As a result, the cycling stability of the $LiMn_2O_4$ electrode is rather poor.

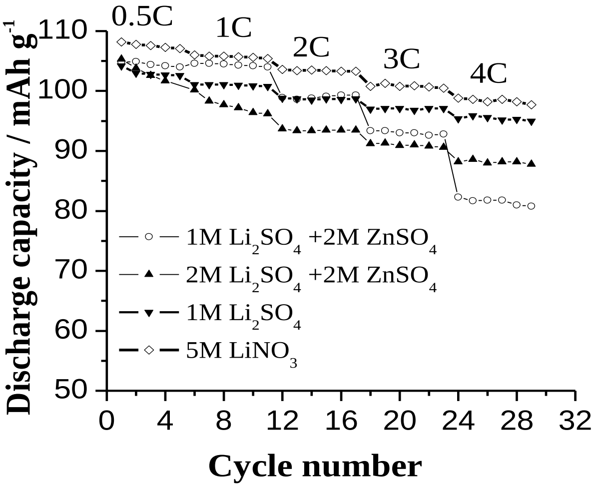
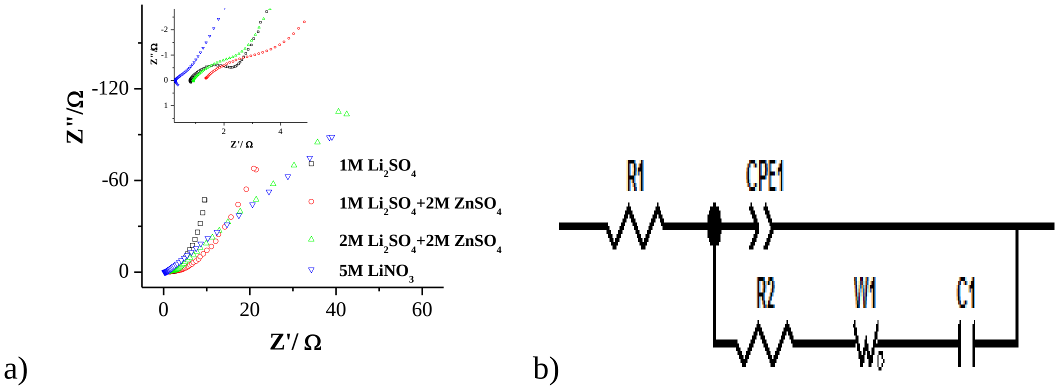


Figure 4. Discharge specific capacities of the $LiMn_2O_4$ electrode in the various electrolytes at different current densities rates.

Fig. 4 shows the discharge specific capacities of the $LiMn_2O_4$ electrode in the various electrolytes at different charge/discharge current rates. The addition of $ZnSO_4$ into the Li_2SO_4 solution does not favor the rate performance of electrodes, whereas an increased Li^+-ion concentration facilitates the enhancement of the specific capacity at a high charge/discharge current rate. For current rates of 0.5-4 C, the specific capacities of the electrodes in the 5 M $LiNO_3$, 1 M Li_2SO_4, 1 M Li_2SO_4 + 2 M $ZnSO_4$ and 2 M Li_2SO_4 + 2 M $ZnSO_4$ solutions are decreased from 108, 104, 104 and 105 mAh g^{-1} to 98, 95, 80.8 and 87.8 mAh g^{-1}, i.e., decreased by 9.3, 8.7, 22.3 and 16.4%, respectively. The rate capabilities follow the order 5 M $LiNO_3$ > 1 M Li_2SO_4 > 2 M Li_2SO_4 + 2 M $ZnSO_4$ > 1 M Li_2SO_4 + 2 M $ZnSO_4$, which is in agreement with the ac impedance results in Fig. 5a. That is to say, the rate dischargeability decreases with the electrode impedance increasing [10]. As shown in Fig. 5a, the Nyquist plots of the four samples show only one semicircle in high and a straight line in low frequency region, which are related to the charge-transfer process and Li^+ diffusion through the bulk of the active material, respectively. In low frequency region This drastic decrease observed in various electrolytes is identical to results reported by Lee and Pyun in saturated LiNO3 solution [12]. The corresponding equivalent circuit is shown in Fig. 5b. In order to obtain better fitting results, the parallel pure capacitor in the equivalent circuit is replaced by a constant-phase element (CPE), when the impedance spectra exhibit low-frequency dispersion. The equivalent circuit consists of a series circuit of two components. It comprises a resistance for charge transfer (R_{ct}), a CPE corresponding to the double-layer capacitance (Q, with a p value of approximately 0.7) and a Warburg element (Z_W) corresponding to lithium ion diffusion in the solid state, as well as a C_{dl} corresponding to the pure capacitance and a resistance (Rs) corresponding to the solution resistance. All the spectra get good fitting results using the same equivalent circuit. The experimental data of $LiMn_2O_4$ electrode in different electrolytes are fitted, the specific data are summarized in Table 2. In the 5 M $LiNO_3$ solution, the $LiMn_2O_4$ electrode exhibits the lowest R_{ct} and R_s values, and the R_w value is relatively low. Thus, the electrode exhibits superior rate discharge ability. The next is the electrode in the 1 M Li_2SO_4 solution.



a) b)

Figure 5. Impedance spectra (a) of $LiMn_2O_4$ electrode as Nyquist plots measured at 25 °C and the corresponding equivalent circuit(b) in different electrolytes.

Table 2. Evaluated impedance parameters according to the equivalent circuit of Fig. 5(B) $LiMn_2O_4$ in different electrolytes.

Electrolytes	Rs	Rct	R_w	C_{dl}
1M Li_2SO_4	0.8	1.63	0.0021	0.4
1M L i_2SO_4+2M $ZnSO_4$	1.32	2.03	1.8	0.25
2M Li_2SO_4+2M $ZnSO_4$	0.89	2.78	0.027	0.11
5M $LiNO_3$	0.28	0.86	0.017	0.068

The addition of $ZnSO_4$ into the 1 M Li_2SO_4 solution significantly increases the AC impedance. However, the increased Li^+-ion concentration effectively decreases the R_s and R_w values, which leads to an enhancement in the rate discharge ability of the $LiMn_2O_4$ electrode.

4. CONCLUSIONS

Using commercial $LiMn_2O_4$ as the active material to prepare electrodes, the effects of the electrolyte on the electrochemical performance of the $LiMn_2O_4$ electrodes were investigated. It is shown that with increased Li^+-ion concentration, the potential of the $LiMn_2O_4$ electrodes shifts to a positive value, improving the kinetics. Anions in the electrolyte exert a great influence on the electrochemical performance of the $LiMn_2O_4$ electrodes, which is mainly associated with Mn dissolution and oxygen evolution. In $LiNO_3$ solutions, the extent of Mn dissolution is minimal and is not dependent on the NO_3^- concentration. Additionally, the overpotential of oxygen is high. As a result, the electrode in the 5 M $LiNO_3$ solution exhibited excellent kinetic characteristics with good rate dischargeability and cyclability. In Li_2SO_4 solutions, the $LiMn_2O_4$ electrode exhibited relatively serious Mn dissolution and the low overpotential of oxygen presents good rate dischargeability, but it shows fast capacity fade during prolonged charge/discharge cycling. The addition of zinc salts into the Li_2SO_4 solution results in an increase in the amount of dissolved Mn due to an increase in the acidity. However, oxygen evolution is effectively prevented, and the cyclability of the $LiMn_2O_4$ electrode is improved. In LiCl solutions, the extent of Mn dissolution is large, and the electrode is affected by simultaneous O_2 and Cl_2 evolution. Although the addition of zinc salts substantially inhibits side reactions, a sharp deterioration in the capacity occurs during charge/discharge cycling.

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