

Electrochemical performance and kinetics of $\text{Li}_{1+x}(\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3})_{1-x}\text{O}_2$ cathodes and graphite anodes in low-temperature electrolytes

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Abstract

Lithium-ion batteries have started replacing the conventional aqueous nickel-based battery systems in space applications, such as planetary landers, rovers, orbiters and satellites. The reasons for such widespread use of these batteries are the savings in mass and volume of the power subsystems, resulting from their high gravimetric and volumetric energy densities, and their ability to operate at extreme temperatures. In our pursuit to further enhance the specific energy as well as low-temperature performance of Li-ion batteries, we have been investigating various layered lithiated metal oxides, e.g., LiCoO_2 , $\text{LiNi}_{0.8}\text{Co}_{0.2}$ and $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$, as well as different low-temperature electrolytes, including ternary and quaternary carbonate mixtures with various co-solvents. In this paper, we report our recent studies on $\text{Li}_{1+x}(\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3})_{1-x}\text{O}_2$ cathodes, combined with three different low-temperature electrolytes, i.e.: (1) 1.0 M LiPF_6 in EC:EMC (20:80), (2) 1.2 M LiPF_6 in EC:EMC (20:80) and (3) 1.2 M LiPF_6 in EC:EMC (30:70). Electrical performance characteristics were determined in laboratory glass cells at different discharge rates and different temperatures. Further, individual electrode kinetics of both $\text{Li}_{1+x}(\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3})_{1-x}\text{O}_2$ cathodes and MCMB graphite anodes were determined at different temperatures, using dc micropolarization, Tafel polarization and electrochemical impedance spectroscopy (EIS). Analysis of these data has led to interesting trends relative to the effects of solvent composition and salt concentration, on the electrical performance and on the kinetics of cathode and anode. Published by Elsevier B.V.

Keywords: Lithium-ion cells; Low-temperature electrolytes; Performance; Kinetics

1. Introduction

Lithium-ion batteries are preferred to the conventional aqueous nickel rechargeable battery systems in several space applications, such as planetary landers [1], rovers [2], orbiters and satellites. The reasons for such widespread use of Li-ion batteries are the benefits in mass and volume, both of which are always critical in any mission, resulting from a three-fold enhancement in the specific energy and about a six-fold benefit in the energy density. In addition, the ability to operate at extreme temperatures greatly simplifies their thermal management. A combination of these desirable attributes of lithium-ion batteries will result in significant enhancement of space missions, or can even be mission enabling in some cases, e.g., the on-going Mars Exploration Rovers.

In order to address the challenges of future missions to ‘Moon, Mars and Beyond’ as envisaged by NASA’s Exploration Systems Mission Directorate (ESMD), we undertook a technology development endeavor to further enhance the specific energy and low-temperature performance of Li-ion batteries. In this pursuit, we have been examining various layered lithiated metal oxides as well as different low-temperature electrolytes [3,4]. Compared to the conventional LiCoO_2 , $\text{LiNi}_{0.8}\text{Co}_{0.2}$ and $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathodes, $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (termed as NMC) cathodes provide higher specific capacity and also enhanced thermal stability. Accordingly, this material is being studied in detail by several research groups, for a range of applications [5–10]. It would be interesting to verify the performance of such cathodes in conjunction with low-temperature electrolytes, and to determine the performance limiting aspects at low-temperature. Given that the rate capability of $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathodes has been reported to be poorer than that of LiCoO_2 cathodes [6,7,10] there is particular interest in determining if the low-temperature capability of

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the material is adversely affected by limited lithium diffusivity. Choi and Manthiram [10] have reported that over 80% of the capacity is maintained at 2 C rates compared to the capacity delivered at C/10, however, the rate capability as a function of temperature and as function of electrolyte type was not investigated.

In this paper, we studied the electrochemical performance of $\text{Li}_{1+x}(\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3})_{1-x}\text{O}_2$, provided by Argonne National Laboratory, in three different low-temperature electrolytes: (1) 1.0 M LiPF_6 in EC (ethylene carbonate):EMC (ethyl methyl carbonate) (20:80, v/v%), (2) 1.2 M LiPF_6 in EC:EMC (20:80, v/v%) and (3) 1.2 M LiPF_6 in EC:EMC (30:70, v/v%), at different discharge rates and temperatures. Even though electrolytes with quaternary solvent mixtures and with ester co-solvents showed impressive low-temperature performance as reported in our earlier publications, the selected electrolytes are also expected to perform well. Besides, the third electrolyte solution is being examined by DoE for hybrid car applications. In addition to the performance at various temperatures, the electrochemical kinetics of the $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathodes as well as the graphitic anodes were determined from dc micropolarization, Tafel and electrochemical impedance spectroscopy (EIS) at various temperatures. Interesting trends have been observed both in terms of the performance and the electrode kinetics at different temperature, as a function of the ratio of EC and EMC and the concentration of the electrolyte salt.

2. Experimental

The cathode and anode materials for these studies contained $\text{Li}_{1+x}(\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3})_{1-x}\text{O}_2$ ($x=0.1$) from Seimi, Japan and MCMB-10-28 graphite from Osaka Gas. The cathodes, coated on Al foil, contained 84% of active material, 8% of conductive diluent and 8% of binder. The anode, on the other hand, had the composition of 90% of active material, 2% of vapor grown carbon fiber (VGCF) as conductive diluent and 8% binder. The electrodes thus supplied by Argonne National Laboratory were trimmed to the size ($\sim 6.5'' \times 1.5''$), bagged with polyethylene separators, and rolled into a jelly roll using Teflon mandrills, which were later inserted into glass cells sealed with O-ring seals. The electrode jelly rolls also had reference electrodes in the form of lithium cold-welded onto Ni foils. The stock solutions for the electrolytes were obtained from EM Sciences, Inc. All the cell fabrication operations were performed in a dry room with less than 1% humidity, while the electrolyte filling or activation was performed in an argon-filled glove box. All the electrochemical performance studies, such as charging, discharging and cycling at different temperatures were carried out using an Arbin battery system and Tenney Jr environmental chambers. For basic electrochemical studies, a combination of an EG&G 273A potentiostat and an EG&G Frequency Response Analyzer was used with the support of a Softcorr program for the dc polarization measurements and a M382 program was used for the electrochemical impedance spectroscopy (EIS) measurements. All measurements were performed at $25 \pm 2^\circ\text{C}$, unless mentioned otherwise.

3. Results and discussions

As mentioned above, the electrochemical performance was determined in the three different electrolytes at various rates of charge and discharge and at different temperatures. To further understand the observed trends in the performance, electrochemical kinetics for both anode and cathode were determined, using dc Tafel and dc micropolarization as well as electrochemical impedance spectroscopy.

3.1. Electrochemical performance

The typical charge–discharge characteristics of one of the three cells during the formation process are illustrated in Fig. 1, in which the cell voltage, anode potential and cathode potential are displayed. As may be seen from this figure, the cell is well balanced, i.e., the cathode and anode capacities are well matched with the selected areas and active material loadings. At the end of charge, the anode potentials remained positive to Li, thus ensuring that there is some buffer in the anode capacity and that there would not be any lithium plating under normal conditions. Table 1 shows further details on the charge and discharge capacities and coulombic efficiency in the first five formation cycles. As may be seen from the figure, all these characteristics are nearly identical for the electrolytes studied here.

Relative to the rate capability at room temperatures, the electrolyte with low salt concentration and low EC-content yielded $\sim 89\%$ of the low rate (0.2 C) capacity at 0.8 C, while the electrolyte with higher salt and low EC gave a capacity of 90.5% and the cell with high salt and high EC gave $\sim 93\%$. Thus, it is clear that high EC formulations, and electrolytes with high salt concentrations, perform better at high discharge rates at ambient temperatures.

Fig. 2 illustrates the performance of these cells at low temperatures, specifically at -40°C and -50°C . The percent capacities under these conditions are also listed in Table 2. As may be seen from the figure, at -40°C using a low discharge rate of C/20, the performance is the best with the electrolyte with high EC-content, while the low EC solution, especially with

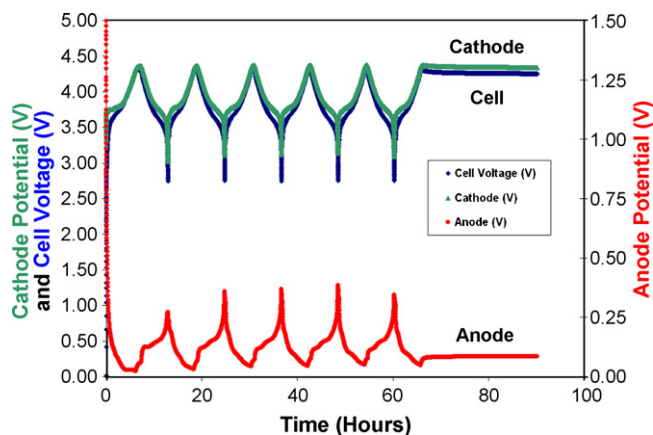


Fig. 1. Charge–discharge curves of $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ -C laboratory test cell with 1.0 M LiPF_6 /EC:EMC (20:80) electrolyte solution during the formation cycles. Also shown are the individual potentials of cathode and anode.

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