Reinvestigation on the state-of-the-art nonaqueous carbonate electrolytes for 5 V Li-ion battery applications

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ARTICLE INFO	ABSTRACT
	The charging voltage limits of mixed-carbonate solvents for Li-ion batteries were systematically investigated from 4.9 to 5.3 V in half-cells using Cr-doped spinel cathode material $LiNi_{0.45}Cr_{0.05}Mn_{1.5}O_4$. The stability of conventional carbonate electrolytes is strongly related to the stability and properties of the cathode materials in the de-lithiated state. This is the first time report that the conventional electrolytes based on mixtures of EC and linear carbonate (DMC, EMC and DEC) can be cycled up to 5.2 V on $LiNi_{0.45}Cr_{0.05}Mn_{1.5}O_4$ for long-term cycling, where their performances are similar. The discharge capacity increases with the charging cutoff voltage and reaches the highest discharge capacity at 5.2 V. The capacity retention is about 87% after 500 cycles at 1C rate for all three carbonate mixtures in half-cells when cycled between 3.0 V and 5.2 V. When cycled to 5.3 V, EC-DMC still shows good cycling performance but EC-EMC and EC-DEC show faster capacity fading. EC-DMC and EC-EMC have much better rate capability than EC-DEC. The first-cycle irreversible capacity loss increases with the cutoff voltage. The "inactive" conductive carbon is also partly associated with the low first-cycle Coulombic efficiency at high voltages due to electrolyte decomposition and possible PF_6^- anion irreversible intercalation.

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1. Introduction

The state-of-the-art (SOA) Li-ion batteries have achieved great success in portable electronics and power tools. They are now starting to enter the electric vehicle (EV) and grid energy storage markets. For EV applications, the SOA Li-ion battery technology can only meet the requirements for short-range applications due to their limited energy density. To further improve the energy density of a Li-ion battery, cathode and anode materials with higher specific capacities and cathode materials with a higher voltage

plateau are required. Some 5 V cathode materials have shown very promising results to enhance the energy density of Li-ion batteries, which include $Li_3V_2(PO_4)_3$ (charged to 4.8 V) [1,2], $LiNi_{0.5}Mn_{1.5}O_4$ and its doped derivatives (4.9 V) [3–10], $LiCoPO_4$ (5.0 V) [11–13], Li_2CoPO_4F (5.5 V) [14,15], and others. However, the high voltage stability of the electrolytes has always been one of the main barriers to the application of these high operating voltage materials.

Previous literature indicates much confusion on the upper voltage limits of the SOA Li-ion battery electrolytes based on organic carbonate solvents. For example, it has been reported that the carbonate electrolytes are not stable at 4.3–4.5 V vs. Li/Li^+ on $LiCoO_2$ and $LiNi_xMn_yCo_zO_2$ (where $x + y + z = 1$) electrodes [16–20]. However, some of the carbonate electrolytes exhibit very good battery performance when used for $LiNi_{0.5}Mn_{1.5}O_4$ materials in the voltage range up to 4.9 V [8,9,21,22]. Therefore, it is necessary to re-evaluate the carbonate-based nonaqueous electrolytes for high voltage Li-ion batteries to clarify the issue. In this work we report our recent findings on the oxidation potential limits of carbonate-based electrolytes when used with Cr-doped $LiNi_{0.5}Mn_{1.5}O_4$ cathode material ($LiCr_{0.05}Ni_{0.45}Mn_{1.5}O_4$). The electrochemical stability and performance of this battery system will also be reported.

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2. Experimental

2.1. Electrolyte and electrode preparation

Battery-grade ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), diethyl carbonate (DEC), and lithium hexafluorophosphate (LiPF$_6$) were purchased from Novolyte Technologies. Lithium foil (0.75 mm thick) was purchased from Alfa Aesar. All chemicals and materials were used as received. Electrolytes of 1.0 M LiPF$_6$ in single-carbonate solvents and carbonate mixtures (EC-EMC, EC-DEC, EC-DMC, all in 3:7 volume ratio) were prepared in an MBraun glove box filled with purified argon.

LiCr$_{0.05}$Ni$_{0.45}$Mn$_{1.5}$O$_4$ was synthesized by ball milling a mixture of Li$_2$CO$_3$, NiO, Cr$_2$O$_3$ and MnCO$_3$ (all from Sigma–Aldrich) in stoichiometric amounts for 4 h followed by a heat treatment at 900 °C for 24 h in air and a further annealing at 700 °C for 8 h. Details on the preparation and characterization of this material were reported elsewhere [23]. A slurry of LiCr$_{0.05}$Ni$_{0.45}$Mn$_{1.5}$O$_4$, Super P® conductive carbon black (SP, from Timcal), and polyvinylidene fluoride (PVDF, Kynar HSV900, from Arkema Inc.) in an N-methyl pyrrolidone (NMP, from Aldrich) solvent was prepared and cast onto an aluminum foil (from All Foils, Inc.). The weight ratio of LiCr$_{0.05}$Ni$_{0.45}$Mn$_{1.5}$O$_4$:SP:PVDF was 8:1:1 and the active material loading was ~4 mg cm^{-2}. After evaporating the NMP, the cathode sheet was pressed at 3000 psi for 1 min, die-cut into disks with a diameter of 1.27 cm, dried at 110 °C under vacuum overnight, and stored in the glove box. For comparison, an electrode sheet of SP-PVDF (1:1 by wt) was also prepared using the same procedures.

2.2. Characterization and computation

The viscosity and ionic conductivity of the electrolytes at room temperature were measured according to previously reported procedures [24]. The viscosity measurement was conducted on a Brookfield DV-II+ Pro Cone/Plate Viscometer at a spindle speed of 10 rpm. The conductivity was measured using an Oakton® 650 Series Multiparameter Meter. Before tests, all instruments were calibrated and the electrolytes were maintained at 25 °C in a constant-temperature oil bath (Brookfield Circulating Bath Model TC-502).

The surface areas of the electrodes were determined by the Brunauer-Emmett-Teller (BET) method, using nitrogen adsorption/desorption collected with a Quantachrome Autosorb 6-B gas sorption system on degassed samples, as described in a previous report [25]. The as-prepared electrodes were placed in a Macrocell (18 × 40 mm sample holder for large sample pieces) and degassed at 25 °C overnight under vacuum. The degassed samples were tested by nitrogen adsorption/desorption at a constant temperature of 77.4 K. The volume of N$_2$ gas that adsorbed unto/desorbed from the surface of samples was measured (isothermally) vs. relative pressure. The surface area was determined from the isotherm using a five-point BET method.

The highest occupied molecular orbital (HOMO) energies were calculated from the optimized geometry via density functional theory using the Becke, 3-parameter, Lee-Yang-Parr hybrid functionals [26–30]. The calculations were performed with the NWChem computational package as reported previously [31]. The selected level of theory represents a good compromise between computational efficiency and accuracy for the study of ground state geometries.

2.3. Electrochemical tests

The electrochemical oxidation stabilities of liquid electrolytes on different substrates were screened by linear sweep voltammetry (LSV) in a beaker cell (inside the glove box) composed of three electrodes. Li metal was used as both reference and counter electrodes. The electrolyte samples on different working electrodes were scanned from the open circle voltage to 6.5 V vs. Li/Li$^+$ at a scan rate of 0.1 mV s^{-1} using a CHI 660C electrochemical workstation (CH Instruments). The cyclic voltammetry (CV) of the LiCr$_{0.05}$Ni$_{0.45}$Mn$_{1.5}$O$_4$ electrode in three electrolytes of conventional carbonate mixtures was tested on a CHI 1000A electrochemical station (CH Instruments) using Li metal as counter electrode. The samples were scanned between 3 V and different cutoff voltages from 4.9 to 5.3 V at a scan rate of 10 μV s^{-1}. All the electrochemical tests were operated at room temperature.

Coin cell kits of CR2032 type were purchased from MTI Corporation. The negative covers, spacers and springs were made of stainless steel 316 (SS-316), and the positive containers were Al-clad SS-316. Whatman® glass fiber B (GF/B) paper with a diameter of 1.91 cm was used as the separator since it has been reported to be stable at high voltages and has no wetting issues with electrolytes containing single cyclic carbonate solvents and EC-DMC mixture [15]. Li/LiCr$_{0.05}$Ni$_{0.45}$Mn$_{1.5}$O$_4$ half-cells with excess electrolyte were assembled on an electric coin cell crimper (from MTI) inside the glove box. The cells were cycled between 3.0 V and different cutoff voltages from 4.9 to 5.3 V at different current rates on Arbin BT-2000 Battery Testers.

3. Results and discussion

3.1. Conductivity and voltammetric behavior of carbonate electrolytes

The SOA nonaqueous electrolytes for Li-ion batteries contain mixtures of cyclic carbonate (EC, PC) and linear carbonates (DMC, EMC, DEC, and so on) for a wide liquid region, low viscosity and high conductivity. The viscosity and ionic conductivity data for the electrolytes of 1.0 M LiPF$_6$ in single- and mixed-carbonate solvents are summarized in Table 1, along with the HOMO energies of the single-carbonate solvents. The apparent ionic conductivity of the electrolyte is related to the reverse effects of the viscosity of the solution and the number of free ions that is associated with the solvent polarity. The electrolyte of 1.0 M LiPF$_6$ in EC has the highest conductivity among the single-carbonate solvents because EC has the highest polarity (dielectric constant of 89.8). The electrolyte of DMC has higher conductivity than that of PC, which is mainly attributed to the much lower viscosity of DMC electrolyte. The electrolytes of 1.0 M LiPF$_6$ in mixed carbonates of EC and linear carbonates, in descending order of conductivity, are EC-DMC > EC-EMC > EC-DEC.

The electrochemical oxidation potentials of these electrolytes have been studied previously on smooth, inert metal (e.g. Pt) and glassy carbon electrodes as well as some real active cathode

Table 1
HOMO energies and physical properties of single-carbonate solvents.

Carbonate	HOMO energy (eV)	1.0 M LiPF$_6$ solution	
		Conductivity at 25.0 °C (mS cm^{-1})	Viscosity at 24.7 °C (cP)
EC	−7.70	8.27	7.74
PC	−7.63	5.65	9.18
DMC	−7.80	6.78	1.20
EMC	−7.30	4.27	2.04
DEC	−7.25	2.87	2.76
EC-DMC[a]	N. A.	11.76	2.64
EC-EMC[a]	N. A.	9.13	4.32
EC-DEC[a]	N. A.	6.90	4.02

[a] Note: The volume ratio of EC to linear carbonate (DMC, EMC or DEC) is 3:7.