

7. Background of Research

The development of sustainable society urgently demands high-performance batteries that can serve as a smooth energy transition from the renewable but intermittent energy sources, such as solar, wind and ocean, into the grid, or an energy storage device to power various consumer devices, such as smart phones, computers and electric vehicles. Lithium ion batteries possess highest energy density among all the batteries developed so far, yet they still cannot satisfy the society's development, which increasingly demands higher energy density and better safety. Even equipped with state-of-the-art lithium-ion batteries, the smart phones cannot run a sufficient time so that they have to be charged frequently, and the electric vehicles generally have a short mileage which causes a range anxiety. Moreover, lithium-ion batteries also suffer from fire and/or explosion, which poses a severe safety problem that threatens the customers' lives and properties, and thus, greatly impedes the large-scale applications of batteries. These above issues are considerably associated with the lithium-ion electrolyte, which was developed in 1990s with a general formula of ~ 1 mol/L solution of LiPF_6 in a mixture of carbonate ester solvents. This electrolyte contains a large amount of free-state solvent molecules that are highly volatile and flammable, which not only causes a severe safety risk but also limits the operation voltage (energy density) of battery. Therefore, it is necessary to develop new electrolytes alternative to conventional lithium-ion electrolyte so as to realize next-generation high-performance batteries. My work in The University of Tokyo is attempting to change the formula of conventional lithium-ion electrolyte with aims to widen its electrochemical window and to improve its safety property.

8. Research methodology

Preparation of electrolytes and electrodes.

Electrolyte solutions were prepared by mixing a given amount of salt with solvents in an Ar-filled glove box. The conventional dilute electrolytes were purchased from Kishida Chemical Co. Ltd and used as the reference.

The electrodes were fabricated by first well mixing the active electrode materials, PVdF binder, and/or conductive carbon (typically, for cathode, 87:5:7; for anode, 90:10:0) in *N*-methylpyrrolidone (NMP). The resultant slurry was cast on the current collector (Al foil for cathode and Cu foil for anode) using a doctor blade. All those electrodes were dried at 120 °C under vacuum for 12 hours. Thin electrodes with the mass loading of active material of $\sim 1 \text{ mg cm}^{-2}$ were used in half-cells; thick electrodes with the mass loading of active material of $\sim 10 \text{ mg cm}^{-2}$ were used in full cells

Electrochemical measurements.

Linear sweep voltammetry (LSV) was performed by VMP-3 (BioLogic) in a three-electrode cell

with an Al belt/foil as a working electrode and lithium metal as the reference and counter electrodes. Half-cells and full cells were assembled in the standard 2032-type coin cell hardware in an Ar-filled glove box. Galvanostatic charge/discharge cycling and rate capability tests were conducted on a charge/discharge unit (TOSCAT). Charge and discharge were conducted at the same C-rate without using a constant-voltage mode at both ends of the charge and discharge.

Characterizations.

The flammability was tested on an electrolyte-soaked glass fibre filter (Advantec GB-100). SEM measurements were performed to observe the morphology of electrode surface using a Hitachi apparatus (S4800) at 3 kV. EDS was applied to estimate the content of transition metals deposited on the graphite anode. XPS was conducted to characterize the surface film of the electrode using an ULVAC PHI 5000 VersaProbe spectrometer with monochromatized Al K α radiation. A charge neutralizer was applied to compensate for the sample surface charge.

Simulations.

Car-Parrinello type density functional theory-based molecular dynamics (DFT-MD) simulations were carried out using CPMD code.³² A fictitious electric mass of 500 a.u. and a time step of 4 a.u. (0.10 fs) were chosen. The temperature was controlled using a Nosé thermostat with a target temperature of 30 °C. After 5 ps equilibration steps, statistical averages were computed from trajectories of at least 10 ps in length. The electronic wave function was quenched to the Born-Oppenheimer surface approximately every 1 ps to maintain adiabaticity. The energy cutoff of the plane wave basis is set to 90 Ry.

9. Results/impacts

9.1. Superconcentrated electrolytes for a high-voltage lithium-ion battery

Finding a viable electrolyte for next-generation 5 V-class lithium-ion batteries is of primary importance. A long-standing obstacle has been metal ion dissolution at high voltages. The LiPF₆ salt in conventional electrolytes is chemically unstable, which accelerates transition metal dissolution of the electrode material, yet beneficially suppresses oxidative dissolution of the aluminium current collector; replacing LiPF₆ with more stable lithium salts may diminish transition metal dissolution but unfortunately encounters severe aluminium oxidation. We propose a new electrolyte design to solve this dilemma. By mixing a highly stable lithium salt with a solvent at extremely high concentrations, we obtained an unusual liquid showing a three-dimensional network of anions and solvent molecules that coordinate strongly to Li⁺ ions (see Figure 1a). This new class of electrolytes inhibited the dissolution of both aluminium and transition metal at around 5 V, and realized a high-voltage LiNi_{0.5}Mn_{1.5}O₄ | graphite battery that exhibited excellent cycling durability,

high rate capability and enhanced safety (see Figure 1b, 1c).

This work received highly positive comments from the reviewer, “It employs LiFSA as salt and a linear carbonate ester DMC as solvent, resulting in a rare formula of single salt/single solvent electrolyte that works in the harshest electrochemical environment that consists of a 5 V cathode and graphite anode...Considering the significant interest in the community in a 5 V class electrolyte, this work represents a breakthrough in the field of electrolyte.” It was published in a top journal of “Nature Communications” and was spotlighted on a leading web-based news service of “Phys.org”. This work has been cited for >70 times since it published on July 2016.

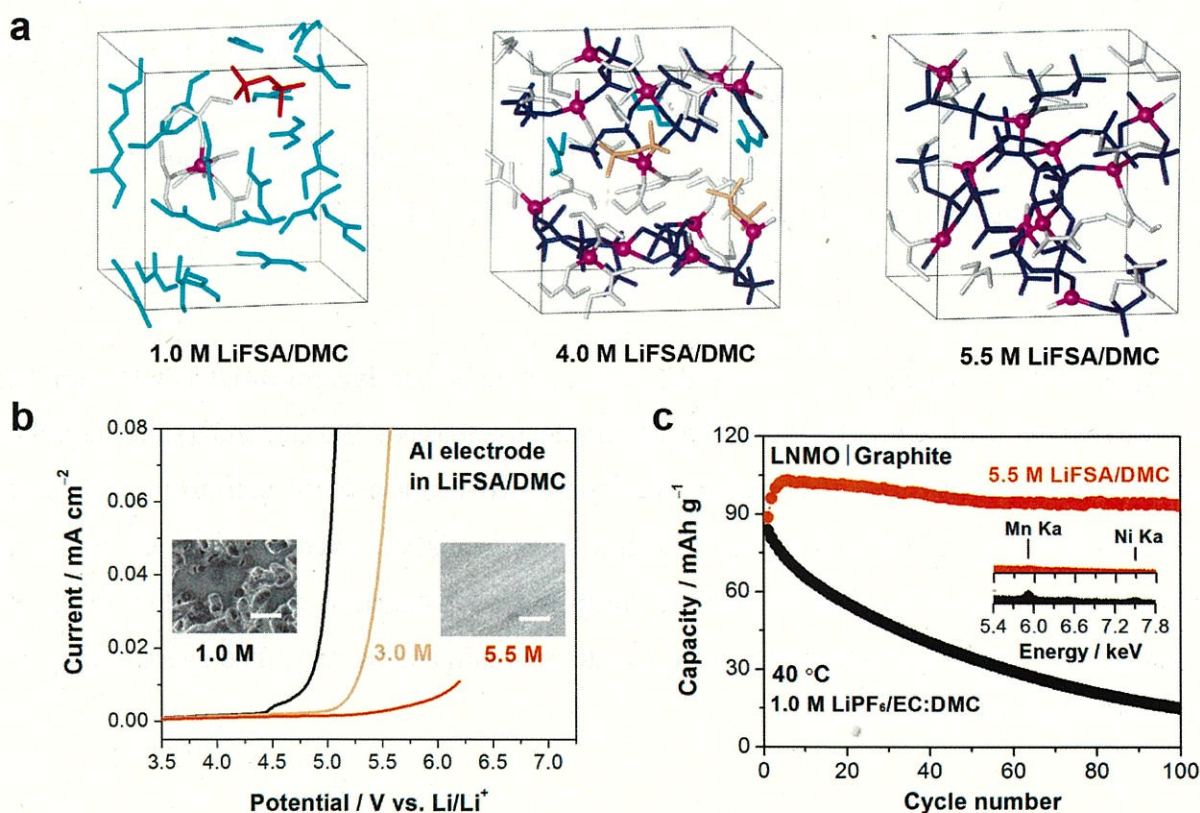


Figure 1. (a) Solution structures obtained by DFT-MD simulations: 1.0 M dilute electrolyte, 4.0 M moderately concentrated electrolyte, and 5.5 M superconcentrated electrolyte. Li cations are marked in purple. Free and coordinated DMC molecules are marked in light blue and grey, respectively. Free, CIP and AGG states of FSA⁻ anions are marked in red, light green and dark blue, respectively. Hydrogen atoms are not shown. The superconcentrated electrolyte show a peculiar structure of three-dimensional network. (b) Linear sweep voltammetry of an Al electrode in various concentrations of LiFSA/DMC electrolytes in a three-electrode cell. The insets are SEM images of the Al surface polarized in the 1.0 M (left of panel) and 5.5 M (right of panel) electrolytes. Clearly, the anodic Al dissolution is effectively suppressed as the concentration increases. In the superconcentrated electrolyte, Al electrode can be stable at potentials above 5 V. (c) Discharge capacity retention of the LiMn_{0.5}Mn_{1.5}O₄ | graphite full cells at a C/5 rate. The inset shows EDS spectra on the graphite electrode surface after cycling tests, from which it indicates no significant transition metals deposited on the graphite surface in the superconcentrated electrolyte. The superconcentrated electrolyte effectively suppresses both Al and transition metal dissolution, and thus, improves the cycling durability of the LiMn_{0.5}Mn_{1.5}O₄ | graphite battery.

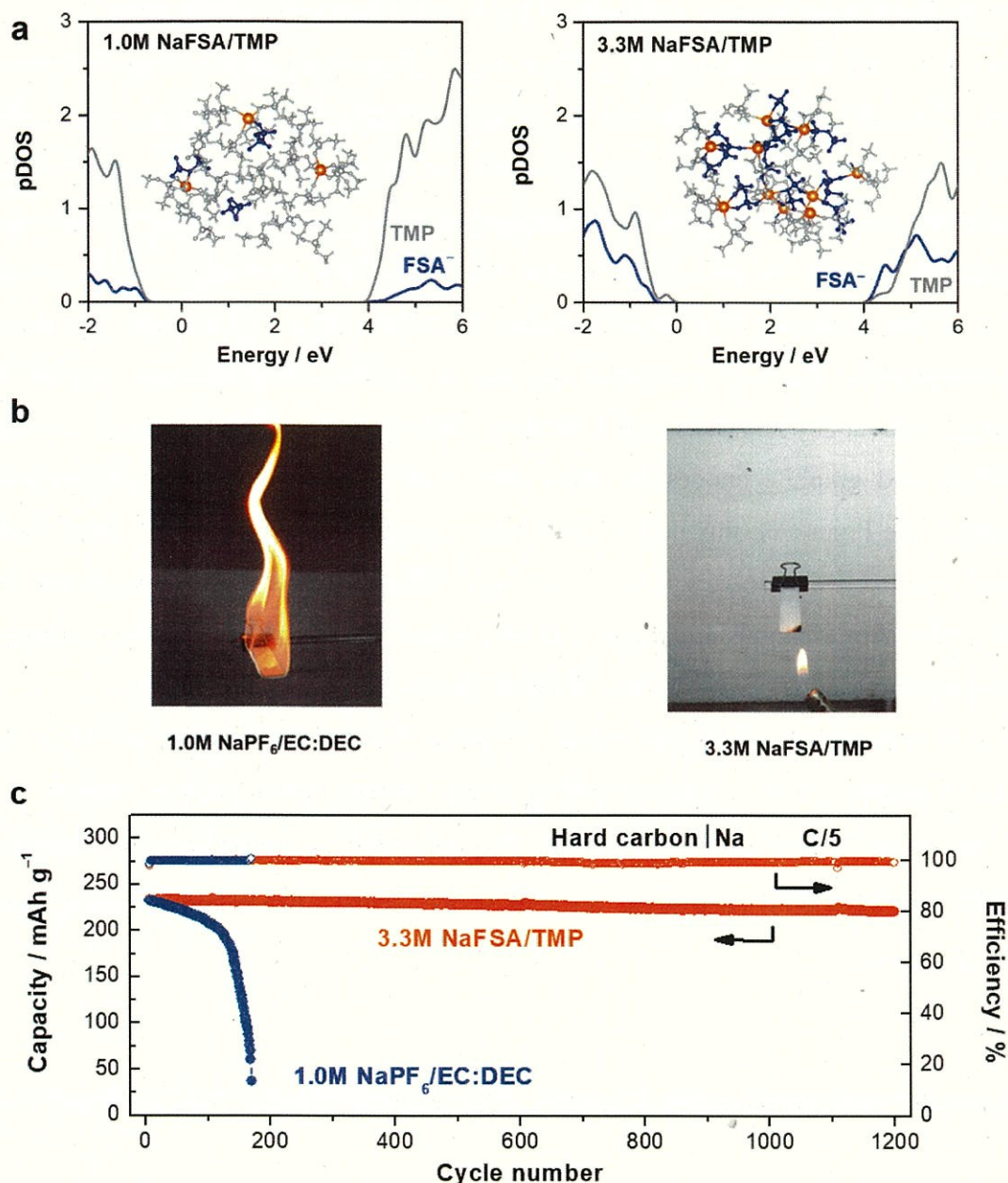


Figure 2. (a) Electronic structures and coordination structures (insets) of dilute 1.0 M and concentrated 3.3 M NaFSA/TMP solutions obtained with DFT-MD simulations. Na⁺ cations, FSA⁻ anions, and TMP solvents are shown in orange, blue, and grey, respectively. It indicated that increasing the concentration from 1.0M to 3.3M leads to the LUMO location shifting from TMP solvent molecules to NaFSA salt, which contributes to the formation of salt-derived passivation film in the concentrated electrolyte. (b) Flame tests of 3.3 M NaFSA/TMP electrolyte and conventional 1.0 M NaPF₆/EC:DEC (1:1 by vol) electrolyte. By excluding all the flammable solvent, the concentrated electrolyte of 3.3M NaFSA/TMP does not support combustion at all, which is totally different from conventional dilute electrolyte. (c) Cycling performance and coulombic efficiency of the hard carbon | sodium metal half-cells using concentrated 3.3 M NaFSA/TMP electrolyte and conventional 1.0 M NaPF₆/EC:DEC (1:1 by vol) electrolyte. The 1200 cycles correspond to a running time of over 15 months. The hard carbon | Na half-cell using conventional dilute electrolyte suffered from a fast capacity decay after 160 cycles because the EC-derived organic passivation film dissolves in the electrolyte in a long-term cycling test. In contrast, the cell using concentrated NaFSA/TMP electrolyte demonstrated an excellent cycling for more than one year, which is due to the formation of a salt-derived inorganic passivation film in the concentrated electrolyte that is much more robust than that in conventional dilute electrolyte.

9.2. Fire-extinguishing organic electrolytes for safe lithium and sodium batteries

Severe safety concerns are currently impeding the large-scale employment of lithium/sodium batteries. Conventional electrolytes are highly flammable and volatile, which may cause catastrophic fires or explosions. Efforts to introduce flame-retardant solvents into the electrolytes have generally resulted in compromised battery performance because those solvents do not suitably passivate carbonaceous anodes. We applied a salt-concentrated electrolyte design to resolve this dilemma via the formation of a robust inorganic passivation film on the anode. We demonstrated that a concentrated electrolyte using a salt and a popular flame-retardant solvent (trimethyl phosphate), without any additives or soft binders, allowed stable charge–discharge cycling of both hard carbon and graphite anodes for more than 1000 cycles (over one year) with negligible degradation (see Figure 2); this performance was comparable or superior to that of conventional flammable carbonate electrolytes. The unusual passivation character of the concentrated electrolyte coupled with its fire-extinguishing property contributes to developing safe and long-lasting batteries, unlocking the limit toward development of much higher energy-density batteries.

This work was published on a top journal of “Nature Energy” and featured as “Cover Image” on the issue of January 2018. It was reported by many internet media, such as English “Chemistry Word”, American “Naked Science”, Australia “Science Alert”, Chinese “Xinhua”, Japanese “日本経済新聞” and “読売新聞”, and so on. We applied one Japanese patent and one international patent based on this work.

10. Research Presentations during the period of the fellowship (Name of the conference, title, place, date)

- [1] International Battery Association (IBA 2017), Superconcentrated electrolytes for a 5 V-class lithium-ion Battery, Nara, Japan, 5th-10th March, 2017
- [2] The 57th Battery Symposium in Japan, Superconcentrated electrolyte for a 5 V-class lithium-ion batteries, Chiba, Japan, 29th November – 1st December, 2016
- [3] 18th International Meeting on Lithium Batteries (IMLB 2016), Superconcentrated electrolytes for a 5 V-class lithium-ion Battery, Chicago, USA, 19th-24th June, 2016.

11. A list of paper published during or after the period of the fellowship, and the names of the journals in which they appeared (Please fill in the format below). Attach a copy of each article if available.

- [1] Jianhui Wang, Yuki Yamada, Keitaro Sodeyama, Eriko Watanabe, Koji Takada, Yoshitaka Tateyama, Atsuo Yamada, Fire-extinguishing organic electrolytes for safe batteries, Nature Energy, Vol. 3, 22-29, 2018. (*Featured as Cover image*)

- [2] Koji Takada, Yuki Yamada, Eriko Watanabe, Jianhui Wang, Keitaro Sodeyama, Yoshitaka Tateyama, Kazuhisa Hirata, Takeo Kawase, and Atsuo Yamada, Unusual passivation ability of superconcentrated electrolytes toward hard carbon negative electrode in sodium-ion batteries, ACS Applied Materials & Interfaces, Vol. 9, 33802-33809, 2017.
- [3] Jianhui Wang, Yuki Yamada, Keitaro Sodeyama, Ching Hua Chiang, Yoshitaka Tateyama, Atsuo Yamada, Superconcentrated electrolytes for a high-voltage lithium-ion Battery, Nature Communications, Vol. 7, 12032, 2016.

Patents

- [1] 特願 2017-215587、山田淳夫、山田裕貴、Jianhui Wang、消火性電解液及び当該電解液を含む二次電池、東京大学、2017 年 11 月 8 日。
- [2] PCT/JP2016075172, Atsuo Yamada, Yuki Yamada, Jianhui Wang, Flame-resistant electrolyte for secondary cell, and secondary cell including said electrolyte, August 16, 2016.

12. Awards during the period of the fellowship (Name of the award, Institution, date etc.)

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