



Short communication

Safe lithium-ion battery with ionic liquid-based electrolyte for hybrid electric vehicles

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ABSTRACT

A lithium-ion battery featuring graphite anode, LiFePO₄-C cathode and an innovative, safe, ionic liquid-based electrolyte, was assembled and characterized in terms of specific energy and power after the USABC-DOE protocol for power-assist hybrid electric vehicle (HEV) application. The test results show that the battery surpasses the energy and power goals stated by USABC-DOE and, hence, this safe lithium-ion battery should be suitable for application in the evolving HEV market.

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1. Introduction

The worldwide demand for clean, low-fuel-consuming transport is promoting the development of safe, high energy and power electrochemical storage and conversion systems. Lithium-ion batteries (LIBs) are today considered the best technology for these applications, a fact also demonstrated by the great interest of hybrid (HEV) and electric vehicle (EV) manufacturers for these batteries. However, conventional lithium-ion batteries combine high energy materials with flammable organic solvents and, hence, can suffer premature failure if subjected to abusive conditions because of heat-evolving, spontaneous reactions which lead to fire and explosion. Safety now represents the main drawback holding up the lithium-ion technology from wide application in HEVs. A very promising class of safe and green electrolytes is that based on ionic liquids (ILs), namely, low temperature molten salts which have important physical chemical properties like high boiling/decomposition points (even over 400 °C), low melting points, thermal and electrochemical stability and appreciable conductivity above RT. This unique combination of favorable properties makes ILs very appealing as safe electrolyte media in lithium-ion batteries, and the PYR₁₄TFSI formed by N-n-butyl-N-methyl-pyrrolidinium cation [PYR₁₄⁺] and N,N-bis(trifluoromethanesulfonyl) imide anion [TFSI⁻] with the

lithium N,N-bis(trifluoromethanesulfonyl) imide (LiTFSI) as dissolved lithium salt is a good choice as an IL-based electrolyte because of the wide electrochemical stability window of this IL [1].

Carbon-coated lithium iron phosphate (LiFePO₄-C) has good thermal stability and specific capacity, so it is the most promising cathode material for safe, high power lithium-ion batteries in the large format modules that are required for power-assist in HEVs [2]. Graphite is the most popular active material for anode production due to its unique characteristics in terms of capacity, cyclability and low voltage of the lithium insertion/deinsertion process, thereby providing high specific energy LIBs. A battery with ionic liquid electrolyte and LiFePO₄ cathode material will be characterized by high safety, and the use of a graphite anode will guarantee the high voltage and, hence, the high energy of the battery. However, unlike the LiFePO₄ cathode, recent studies have demonstrated that the graphite anode in pyrrolidinium-based IL electrolyte requires the use of an additive in the electrolyte solution like vinylencarbonate (VC) for SEI formation because this IL does not display film-forming ability on graphite [3,4].

We report the results of electrochemical tests on a graphite/LiFePO₄ lithium-ion battery with electrode balanced in capacity and with PYR₁₄TFSI-LiTFSI 0.4m electrolyte added with 10% (w/w) of VC. The results include battery characterization on the basis of the United States Advanced Battery consortium (USABC) and Department of Energy (DOE) FreedomCAR protocol to simulate the dynamic functioning of the battery in power-assist full HEV [5–7]. The electrochemical stability of the battery evalu-

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Table 1

Viscosity (η) and conductivity (σ) data of $\text{PYR}_{14}\text{TFSI}$ 0.4 m LiTFSI with 10% VC, $\text{PYR}_{14}\text{TFSI}$ 0.4 m LiTFSI and EC DMC- LiPF_6 1 M.

Electrolyte	η/cP (at °C)	$\sigma/\text{mS cm}^{-1}$		
		30 °C	50 °C	60 °C
$\text{PYR}_{14}\text{TFSI-LiTFSI}$ 0.4 m	178 (24.1)	1.7	3.6	5.3
$\text{PYR}_{14}\text{TFSI-LiTFSI}$ 0.4 m 90%+ VC 10%	62 (23.5)	4.4	7.9	9.8
EC DMC LiPF_6 1 M	4 (25.3)	12.5	16.5	18.5

ated over long cycling and the characterization for HEV application repeated after cycling are also reported.

2. Experimental

The LiTFSI (3 M) salt was dissolved in ionic liquid $\text{PYR}_{14}\text{TFSI}$ (Solvent Innovations) in order to obtain a salt concentration of 0.4 m and then the VC (97%, Fluka) was added to obtain an IL electrolyte with 10% (w/w) VC. The viscosity and conductivity measurements were performed by a Micro-Ubbelohde viscosimeter and by a Radiometer Analytical CDM210 Conductivity meter, respectively.

$\text{LiFePO}_4\text{-C}$ was synthesized as in Ref. [2]. $\text{LiFePO}_4\text{-C}$ composite electrodes were prepared by lamination on carbon-coated aluminum grid (Lamart) of a paste obtained by mixing 80 wt.% $\text{LiFePO}_4\text{-C}$, 15 wt.% carbon conducting additive (SuperP, MMM Carbon Co.) and 5 wt.% polytetrafluoroethylene (Du Pont, 60 wt.% water dispersion) binder in a small amount of ethanol; the electrodes were dried at 80 °C under vacuum overnight before use. The geometric electrode area was 0.61 cm² and the composite mass loading was 5.4 mg cm⁻² of geometric area. Graphite anode material was a commercial product Timrex KS-15 (TIMCAL), and the electrodes were prepared by “doctor-blade” technique. A slurry of the following composition: graphite:SuperP:PVDF = 70:10:20 wt.%, was prepared and coated onto a porous copper foil (Schlenk, thickness 0.01 mm) current collector using the doctor blade and dried at 120 °C under vacuum overnight. Circular electrodes were cut from the foil with a geometric area of 0.61 cm² and the composite mass loading was 5.0 mg cm⁻² of geometric area. “T-type” electrochemical cells with Li reference electrode were used for battery characterization. A dried and degassed glass separator (Durieux 200 μm thick when pressed) was used after soaking in the same electrolyte of the electrochemical cell. Cell assembly and sealing were performed in an argon atmosphere MBraun Labmaster 130 dry box (H_2O and $\text{O}_2 < 1$ ppm) and the electrochemical tests were performed in a Thermoblock (FALC) oven at 60 °C using a Perkin-Elmer VMP multichannel potentiostat.

3. Results and discussion

The results of the viscosity and conductivity measurements of the prepared electrolyte $\text{PYR}_{14}\text{TFSI-LiTFSI}$ 0.4 m with 10%VC, compared with those of the same electrolyte without VC and of the conventional electrolyte EC DMC 1:1 LiPF_6 1 M, are reported in Table 1. As expected the conductivity is related to the viscosity of the electrolyte because the latter affects ion mobility; thus, the addition of VC to the IL increases the conductivity as a consequence of the decrease of viscosity.

The battery was composed of a $\text{LiFePO}_4\text{-C}$ cathode, graphite anode and $\text{PYR}_{14}\text{TFSI}$ 0.4 m LiTFSI with 10%VC electrolyte, and the electrodes were balanced in capacity. Given that graphite has an irreversible capacity that in the first cycle is significantly higher than lithium iron phosphate, the single electrodes were pre-cycled vs. lithium in the same electrolyte at 60 °C for a few cycles in order to achieve a high efficiency (i.e. high charge/discharge reversibility) and then were assembled in battery configuration. The separator of

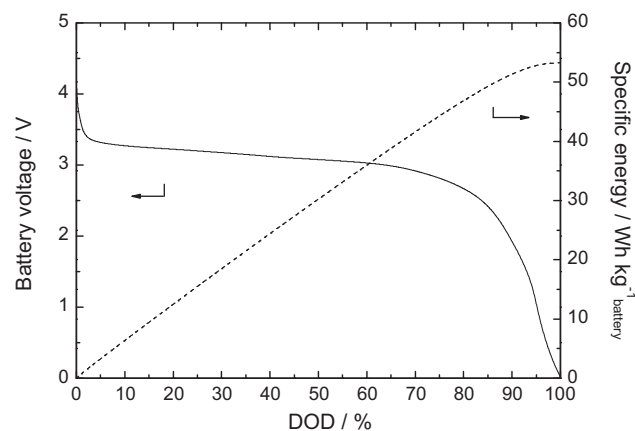


Fig. 1. Battery static capacity test (SCT) at 1C-rate and 60 °C. Dashed line is the relationship between cumulative energy and DOD.

each electrode was maintained in the battery assembly to preserve electrode integrity and, so, the cell had two separators.

The battery was characterized by USABC-DOE benchmark tests to simulate dynamic battery functioning in power-assist full HEV, where the battery is used during acceleration for a short time and kept within a DOD range (never approaching the fully charged or fully discharged state) by regenerative braking or the engine. The tests included a static capacity test (SCT) at 1C discharge rate and a hybrid pulse power characterization (HPPC) test, which together provided the battery dynamic-power capability over available energy. The HPPC test incorporates both discharge and regenerative pulses: the battery is first discharged for 10 s at the stated C-rate, then allowed to relax to OCV for 40 s, and finally charged for 10 s with a regenerative pulse at 75% current of the discharge pulse. A voltage limit (V_{\min}) for discharge pulse corresponding to 55% of the maximum (V_{\max}) voltage for regenerative pulse is recommended. The sequence is repeated, from 10% to 90% DOD, with a 10% increment through discharge steps at 1C-rate, each followed by a 1-h rest period before applying the next sequence. The HPPC test begins with a fully 1-C charged battery after 1 h OCV rest and ends before 90% DOD if the battery voltage exceeds the V_{\max} in regenerative or V_{\min} in discharge pulse. The results of the SCT and HPPC tests are used to plot the available energy vs. pulse power capability and evaluate whether the battery matches the target for power-assist full HEV.

The tests of the lithium-ion battery we assembled were performed by setting the V_{\max} at 3.6 V and the V_{\min} at 2.0 V. The 1C discharge for SCT and HPPC tests was practical, i.e. the battery was discharged in 1 h (as suggested in the FreedomCAR manual), while the 5C rate used in the discharge pulses of HPPC test referred to the theoretical capacity of the cathode. All the tests were performed on the battery at 60 °C, and all the evaluated specific parameters refer to a total battery mass (w_{battery}) that is twice the sum of composite electrode mass of the two electrodes. We made this assumption following Ref. [7], though the current collector mass was not included because the battery design was not optimized. Fig. 1 shows, according to the SCT test, the plots of the battery discharge voltage and of the specific cumulative energy removed during discharge (E_{DOD}) vs. DOD at 1C-rate and 60 °C.

Fig. 2 displays the voltage profile of the battery and of each electrode vs. Li reference electrode along the sequence of HPPC test at different DOD from 10% to 70%, separated by 10% DOD. The 10 s pulse discharge and regenerative currents were 3.45 and 2.60 mA cm⁻², respectively. The HPPC test stopped after 70% DOD because the battery voltage reached V_{\min} .

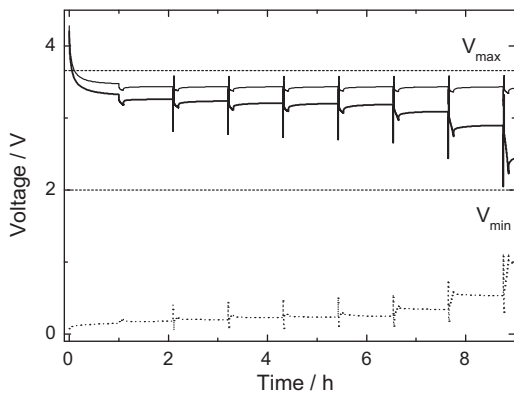


Fig. 2. Voltage profiles of the HPPC performed on the fresh battery. (—) Battery voltage, (---) cathode and (...) anode voltages.

The battery voltage-drop values were used to calculate the discharge and regenerative pulse resistances and, then, the specific discharge (P_{disc}) and regenerative (P_{reg}) pulse power capabilities at each DOD by Eqs. (1) and (2):

$$P_{disc} = \frac{V_{min}(OCV_{disc} - V_{min})}{(R_{disc}W_{battery})} \quad (1)$$

$$P_{reg} = \frac{V_{max}(V_{max} - OCV_{reg})}{(R_{reg}W_{battery})} \quad (2)$$

where OCV_{disc} is the open circuit voltage before the discharge pulse and OCV_{reg} is that before the regenerative pulse. Fig. 3a shows the resistance values, R_{disc} and R_{reg} , vs. DOD calculated from HPPC test of the fresh battery, and Fig. 4 the corresponding pulse power capability values, P_{disc} and P_{reg} , from 10% to 70% DOD vs. cumulative energy. Fig. 4 also displays the minimum pulse power goal stated by DOE FreedomCAR for power-assist HEV.

The power capability vs. energy plot compared with the HEV pulse power target (625 $W\ kg^{-1}$ for discharge and 500 $W\ kg^{-1}$ for charge) indicates that the graphite/PYR₁₄TFSI 0.4 m LiTFSI with 10% VC/LiFePO₄-C lithium-ion battery surpasses the pulse power goal in the range 10–55% DOD, and this is the state of charge in which the battery should be maintained during its use in power-assist mode

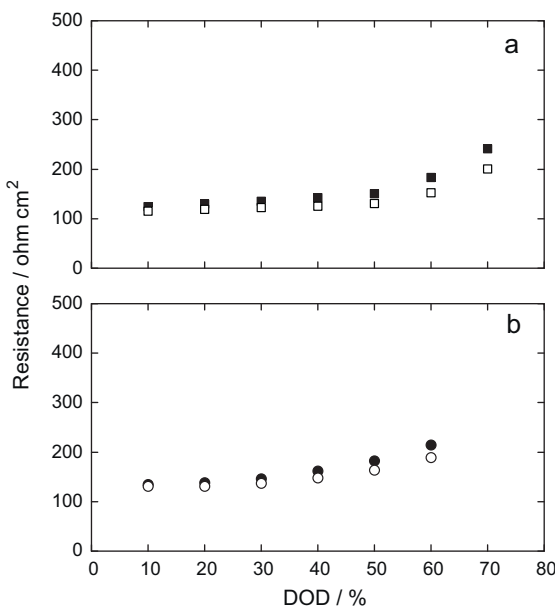


Fig. 3. Pulse resistances vs. %DOD: (a) R_{dis} (■) and R_{reg} (□) calculated from the HPPC test on the fresh battery; (b) R_{dis} (●) and R_{reg} (○) calculated from the cycled battery.

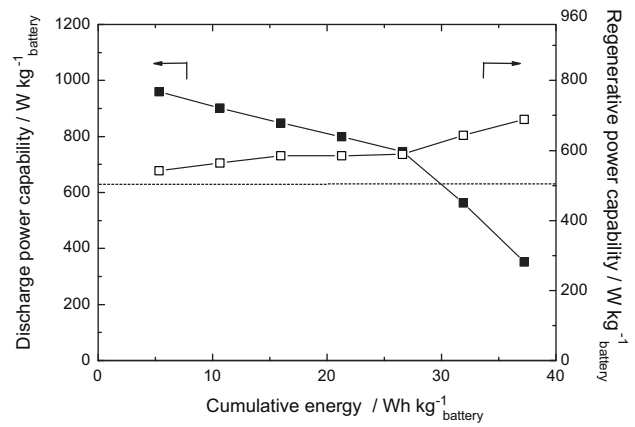


Fig. 4. Discharge power capability vs. energy removed at 1C rate of fresh battery from HPPC test. The dashed line refers to HEV pulse power target.

in HEV. The corresponding available energy between these DODs is 25 $Wh\ kg^{-1}_{battery}$, well above the DOE target (7.5 $Wh\ kg^{-1}_{battery}$). Therefore, this battery surpasses the DOE energy and power goals for power-assist HEV application.

A clear representation of battery performance is given by the plot usable energy vs. power in Fig. 5 (straight line for the fresh battery), where the usable energy is the amount of energy available for a given pulse-power. It represents the energy (or power) available over the operating region where a specified power (or energy) demand can be met. The resulting available energy for the fresh battery at the goal power is 25 $Wh\ kg^{-1}_{battery}$ and the resulting available power at goal energy is 726 $W\ kg^{-1}_{battery}$.

After the SCT and HPPC tests, the battery was repeatedly cycled by deep galvanostatic charge–discharge cycles at 1C to evaluate its cycling stability and then the SCT and HPPC tests were performed again to evaluate the energy and power performance of the battery after long cycling. Fig. 6 reports the discharge capacity of the battery over all the cycles referred to the capacity of the first cycle (the specific capacity of the LiFePO₄ at the first cycle was 85 $mAh\ g^{-1}$ at 1C) and the charge–discharge efficiency values. The capacity fade after 275 cycles was 55%, but the capacity seems to stabilize in the end, and the efficiency values were higher than 99%.

The results of the HPPC test performed on the cycled battery are reported in Fig. 3b (pulse resistance vs. DOD), Fig. 7 (discharge power capability vs. energy removed at 1C rate) and Fig. 5 (usable energy vs. pulse-power, dashed line) and demonstrate that even after long cycling the battery still satisfied the DOE energy and

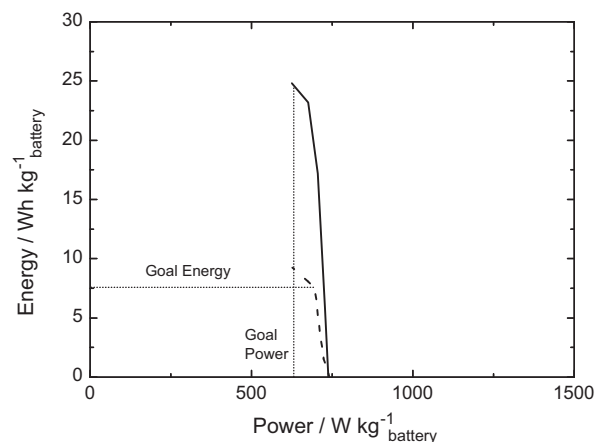


Fig. 5. Usable energy as a function of discharge pulse-power for the fresh (—) and cycled (---) battery. The dotted lines indicate the DOE goals.

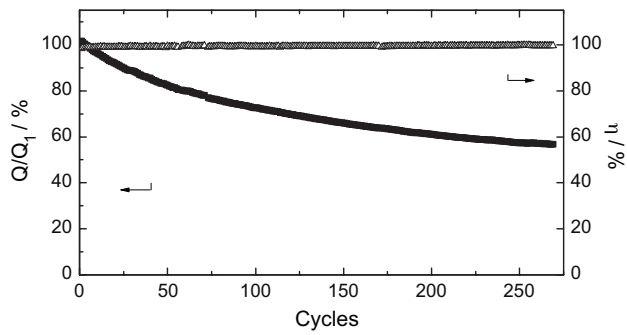


Fig. 6. Battery discharge capacity (normalized to capacity of the first cycle after DOE tests) and efficiency vs. cycle number of the battery cycled at 1C and 60 °C.

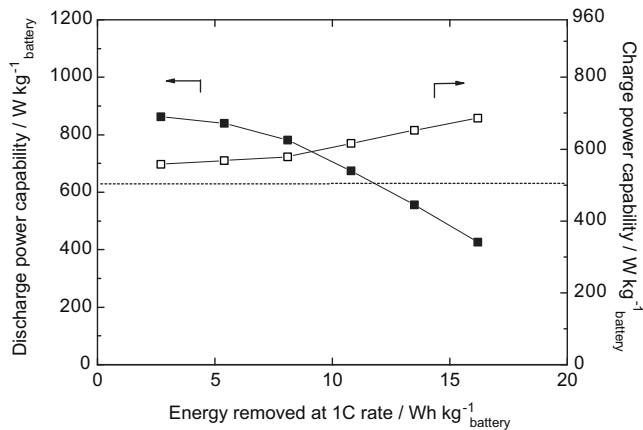


Fig. 7. Discharge power capability vs. energy removed at 1C rate of cycled battery from HPPC 5C test. The dotted line refers to HEV pulse power goal.

power targets for HEV application. The cycled battery surpasses the pulse power goal in the range 10–45% DOD and the corresponding

available energy between these DODs is $9 \text{ Wh kg}^{-1}_{\text{battery}}$, still above the DOE target ($7.5 \text{ Wh kg}^{-1}_{\text{battery}}$). It is worth noting that the pulse power values for fresh and cycled cells are similar because of the comparable pulse resistance values, whereas the available energy decreased after cycling.

4. Conclusions

Our study results of a graphite/LiFePO₄-C lithium-ion battery working with a safe, innovative electrolyte PYR₁₄TFSI 0.4 m LiTFSI 90%:10 wt.% vinylene carbonate, the latter added as SEI-forming component for the graphite electrode, demonstrate that this battery surpasses HEV targets at the beginning of its life and even after long cycling. It is worth noting that this is the first time that practical data of the dynamic functioning of a safe lithium-ion battery working with an ionic liquid-based electrolyte are reported and the results should be relevant for the evolving large-size battery market for HEV application.

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