Nano Energy 47 (2018) 35–42

Contents lists available at ScienceDirect

Nano Energy

journal homepage: www.elsevier.com/locate/nanoen

Full paper

"Tai Chi" philosophy driven rigid-flexible hybrid ionogel electrolyte for high-performance lithium battery

Nan Chen[a,b], Yi Xing[b], Lili Wang[a], Fan Liu[a], Li Li[a,c], Renjie Chen[a,b,**], Feng Wu[a,c], Shaojun Guo[b,d,e,f,*]

[a] School of Materials Science & Engineering, Beijing Key Laboratory of Environmental Science and Engineering, Beijing Institute of Technology, Beijing 100081, China
[b] Department of Materials Science and Engineering, College of Engineering, Peking University, Beijing 100871, China
[c] Collaborative Innovation Center of Electric Vehicles in Beijing, Beijing 100081, China
[d] BIC-ESAT, College of Engineering, Peking University, Beijing 100871, China
[e] Beijing Key Laboratory for Magnetoelectric Materials and Devices (BKL-MEMD), Peking University, Beijing 100871, China
[f] Department of Energy and Resources Engineering, College of Engineering, Peking University, Beijing 100871, China

ARTICLE INFO

Keywords:
Solid-state electrolyte
Ionogel
Ionic liquid
Li metal battery
Tai Chi

ABSTRACT

Dendritic growth of Li metal and its related safety issue in a liquid electrolyte greatly hinder the development of Li metal batteries. Herein, inspired by the Tai Chi philosophy of keeping rigid and flexible balance, we demonstrate a new rigid-flexible hybrid ionogel electrolyte composed of TiO_2 rigid framework, PVDF-HFP flexible framework and LiTFSI-Py13TFSI ionic liquid for greatly boosting the performance of Li battery. The as-made hybrid ionogel electrolyte not only has excellent electrochemical properties, such as ionic conductivity up to 7.4×10^{-3} S/cm at 25 °C and anodic stability up to 5.5 V *versus* Li/Li^+, but also has a high mechanical strength to withstand extrusion. These important features make it be able to realize the stable stripping/plating of Li anodes. The hybrid ionogel electrolyte enables the assembled $LiFePO_4$/Li batteries to be successfully cycled at wide C rate (0.1–2.0 C) and exhibit no significant capacity degradation for up to 500 days (about 600 cycles) at a 0.1 C rate. The design from Tai Chi philosophy to protect Li metal opens new opportunities to realize high energy-density Li metal batteries.

1. Introduction

Rechargeable Li based batteries are currently the most attractive electrochemical energy storage technology because they offer high energy and power densities, which make them dominate the marketplace for the foreseeable future. Li metal anodes are highly promising to replace the commercially used carbonaceous anodes, because Li metal would boost the specific capacity by more than one magnitude [1,2]. Furthermore, the utilization of Li metal anodes can improve the voltage of batteries and reduce the total weight of batteries. A major concern associated with lithium metal is the growth of Li dendrites over successive charge/discharge cycles, which may render internal short circuits, and accelerate detrimental reactions with the electrolyte [3]. Several strategies have been proposed to solve the Li dendrites issue. One interesting direction is the host materials design for Li anode. The well-demonstrated host materials include polyimide [4], polyacrylonitrile fiber [5], nickel foam [6], SiO [7], lithiophilic graphene oxide [8] and grapheme [9], which have the function of suppressing the growth of Li dendrites and alleviating the large volume changes during plating/striping process. Another interesting strategy is the electrolyte formulation, including *in situ* formation of a solid electrolyte interphase (SEI) on Li anode using electrolyte additives [10–12], special Li salts [13,14], and highly concentrated Li salts [15–17]. However, the low electron/ion conductivity and poor mechanical stability of most SEI layers usually make them be only effective for stabilizing a few hundred cycles.

Solid electrolytes have long been understood as attractive candidates since they can mechanically block the growth of Li dendrites. This mechanical blocking idea is consistent with the results form theoretical analysis by Monroe and Newman [18]. They employ linear elasticity theory to compute the additional effect of bulk mechanical forces on electrode stability, showing that a solid electrolyte with shear modulus can mechanically suppress the dendrites effectively. However, solid electrolyte has some drawbacks such as low temperature conductivity

* Corresponding author at: Department of Materials Science and Engineering, College of Engineering, Peking University, Beijing 100871, China.
** Corresponding author at: School of Materials Science & Engineering, Beijing Key Laboratory of Environmental Science and Engineering, Beijing Institute of Technology, Beijing 100081, China.
E-mail addresses: chenrj@bit.edu.cn (R. Chen), guosj@pku.edu.cn (S. Guo).

https://doi.org/10.1016/j.nanoen.2018.02.036
Received 8 January 2018; Received in revised form 15 February 2018; Accepted 19 February 2018
Available online 21 February 2018

and high electrode/solid electrolyte interfacial resistance, typically requiring impractically high operating temperatures for stable battery cycling [19,20]. Although some sulfide-based and garnet-type solid electrolytes have comparable ionic conductivities to that of liquid electrolytes, Li dendrite growth through the grain boundaries is still a major issue [21].

To construct a room-temperature solid Li metal battery, an electrolyte with high conductivity and mechanical strength is highly desirable. Confining ionic liquid into polymer or inorganic host materials, termed as ionogel electrolyte, is introduced [22–24]. Ionogels are now recognized as effective electrolytes to improve the overall performance of lithium metal electrodes. Ionogel electrolytes, combining the benefit of rigid frameworks such as SiO_2 [25,26], TiO_2 [27,28], or IL-tethered SiO_2 [22,29] and liquid, exhibit excellent long-life stability for Li metal batteries. Because the brittle nature of inorganic framework, the progressing dendrites may create cracking in the block ionogel, resulting in short circuit of batteries. Polymers framework possesses lower mechanical moduli than inorganic framework, they offer greater flexibility to fit the dendrite proliferation. But batteries with the ionic liquid-based polymer electrolytes usually exhibit poor cyclic and power performance compared to those made with conventional organic solvent-based polymer electrolytes [30,31], even though they exhibit similar ionic conductivities.

Herein, we refer to Tai Chi philosophy to design a new rigid-flexible hybrid ionogel electrolyte, comprising flexible PVDF-HFP framework, rigid TiO_2 framework, and ionic liquid electrolyte for greatly boosting the performance of lithium metal batteries. The prepared hybrid ionogel electrolyte was free standing and mechanically stability. Their mechanical and electrochemical properties could be tuned by modifying the formulations. TiO_2 rigid framework enlarged the amorphous region of the PVDF-HFP framework, increases the Li^+ conductivity to 7.4×10^{-3} S/cm 25 °C. The rigid-flexible feature of framework and the liquidity of ionic liquid benefit stable lithium electrodeposition and reduce the interface resistance of electrode/electrolyte. The hybrid ionogel stabilized the electrodeposition of lithium over 800 h of repeated stripping/plating at a current density of 0.1 mA/cm^2. The assembled quasi-solid $LiFePO_4$/Li batteries were successfully operated in a series of C rate and run for 500 days at 0.1 C rate with a stable capacity of 150 mAh/g at room temperature. In addition, the hybrid ionogel is a kind of promising electrolyte for application in practical Li metal batteries.

The design concept for the new electrolytes configuration is show in

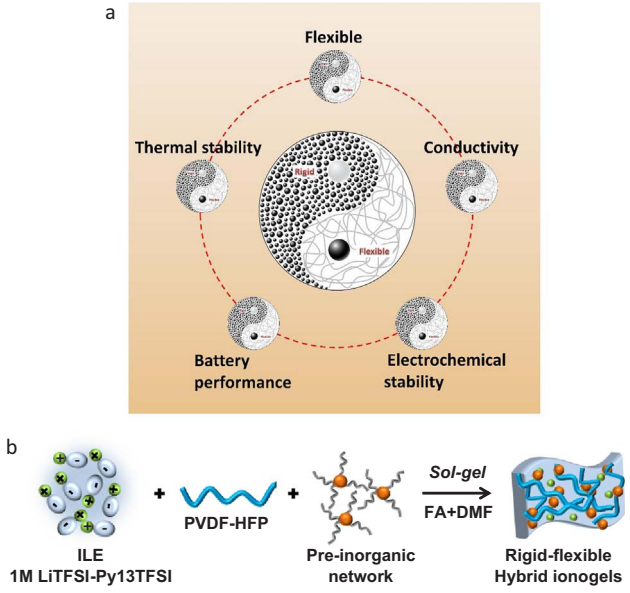

Fig. 1. a) New concept of hybrid ionogel electrolyte. **b)** Preparation process of hybrid ionogel.

Fig. 1**a**. Tai chi as a treasure of Chinese cultural history bears Chinese cultural development of the Taoist concept of ideology and culture. Tai chi map is a symbol of the natural world together. Yin and yang are two opposing principles in nature, and the whole concept of tai chi is about keeping a balance between yin and yang. The hybrid ionogel is composed of yin-yang matrix and an ionic liquid, where the yin and yang represents a flexible framework and rigid framework, respectively. The overall properties of hybrid ionogel are not simply the sum of the individual contributions of their components, but more impacted by the strong synergy. The hybrid ionogel was prepared through a non-hydrolytic sol-gel route, in which ionic liquid electrolyte [ILE, N-methyl-N-propylpyrrolidinium bis(trifluoromethanesulfonyl)imide (Py13TFSI) with a 1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI)] was used as solvent, a mixture of tetrabutyl titanate (TBOT) was used as precursor of TiO_2 rigid framework and a poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVDF-HFP) was used as flexible framework. The whole reaction processes undergo room temperature hydrolysis, mesothermal nonhydrolytic polycondensation (50–80 °C), and *in-situ* confinement of ionic liquid into the rigid-flexible framework (Fig. 1**b**).

A series of hybrid ionogel electrolytes (Table S1) with the modulated PVDF-HFP/TBOT mass ratio in the form of 0/100, 25/75, 50/50, 75/25 and 100/0 were made, and named as N0, N25, N50, N75 and N100, respectively. The increase of the ILE mass percentage would improve the ionic transport ability, but self-standing electrolyte cannot be formed when the mass percentage exceeds a certain limit. In order to make sure that the hybrid ionogel electrolytes had satisfactory electrochemical performance and suitable mechanical property, the hybrid ionogel electrolytes with ILE mass percentage of 90 wt%, 70 wt% and 50 wt% were made. Ternary phase diagram of hybrid ionogel electrolytes is shown in Fig. 2**a**. The three corners of the triangle indicate pure phases for TiO_2, PVDF-HFP and ILE, respectively. Notably, formulations can lead to very different mechanical and electrochemical properties. Formulations within a blue area of the ternary phase space yield a class of rigid hybrid ionogel. These hybrid ionogel were found to be quite brittle (Fig. 2**b**). As one would expect, the mechanical property of hybrid ionogel electrolyte became flexible with increasing PVDF-HFP/TBOT ratio (green area in Fig. 2**a**). These hybrid ionogel deform readily in response to slight pressure (Fig. 2**c**). TiO_2 is known to be particularly effective in confining the flow of ionic liquids [28,32]. The sample containing only TiO_2 framework (sample N0) maintains the fragility of ceramic material and good electrochemical properties of ionic liquid. N75 combines high ILE mass percentage with the suitable mechanical properties required for fabrication of coin cells, which would be our focus in the following electrochemical test.

The samples with and without TBOT are white opaque and transparent, respectively (Fig. 3**a**). The sample with only TBOT shows typical porous morphology after removing the ILE [33,34] (Fig. S1a). The sample with only PVDF-HFP tends to stick together and form porous layer after the evaporation of solvent, N,N-dimethylformamide (See Fig. S1b). The mechanical flexibility of the hybrid ionogel as a self-standing block was measured using an extrusion test. When combining TBOT and PVDF-HFP, the flexion angle of N75 is up to 90° without breaking. What is more, it offers flexibility and well-tuned deformation characteristics under extrusion condition (Fig. 3**b**). The scanning electron microscopy (SEM) image of N75 that the TiO_2 particles and PVDF-HFP framework are uniformly hybrided (Fig. 3**c**). Some sub-micrometer pores were also observed. Fig. 3**d** shows the structural schematic diagram of hybrid ionogel electrolytes. When hybrid ionogel electrolyte contains higher content of TBOT (Fig. S1c&d), excessive TiO_2 nanoparticles would be formed, leading to a large number of pores blocked.

Fourier transform infrared (FT-IR) spectra of ILE, PVDF-HFP and TiO_2 are shown in Fig. S2 and Table S2. Typical peaks of Ti-O-Ti emerge at 400–800 cm^{-1} [35]. The presence of the peaks at 400–800 cm^{-1} in N0 sample after removing the ILE confirms that TiO_2 was successfully synthesized. The FT-IR spectra of PVDF-HFP exhibit the characteristic absorption of its α-phase (532, 614,762,795 and 976 cm^{-1}) and β-