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Current trends and future challenges of electrolytes for sodium-ion batteries

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ABSTRACT

Research and development efforts on sodium-ion batteries are gaining momentum due to their potential to accommodate high energy density coupled with relatively lower cost in comparison with lithium-ion batteries. In order for the sodium-ion batteries to be commercially viable, high performance electrolytes with acceptable ambient temperature ionic conductivity and wider electrochemical stability windows are being developed. A bibliometric analysis of the publications on various types of Na^+ ion conducting electrolytes since 1990 shows a total of 200 + publications and reveals an exponential growth in the last few years, due to reasons that the sodium-ion systems promise great potential as the future large scale power sources for variety of applications. This review consolidates the status of liquid (non-aqueous, aqueous and ionic), polymer gel and solid (ceramics, glasses, and solid polymers) electrolytes and discusses their ionic conductivity, thermal characteristics, electrochemical stability and viscosity towards applications in sodium-ion batteries. Among various types available, the non-aqueous solvent based electrolyte is the most promising one in terms of ionic conductivity even though it is flammable.

Introduction

Since energy is one of the primary concerns in the present day technological world, research and development activities of the renewable energy sector are quickly growing due to the dwindling of fossil fuels. Due to the intermittent nature of these renewable energy sources, energy storage devices such as rechargeable batteries play an important role. Since the commercialization of lithium-ion rechargeable batteries (LIBs) in 1991, they are being used in portable electronic (such as phones, camcorders, tablets and laptops), automotive applications due to their highest energy density values compared to all other battery chemistries. Although, there are several advantages with LIBs, they are relatively expensive and the present cost of lithium resources has almost been doubled compared to that in 1991 [1]. Lithium deposits are mainly distributed in South America (70% of the global deposits) [2],

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causing the lithium battery market to depend on the import of raw lithium materials [3], and also the limited reserves of lithium is not sufficient to meet the ever-increasing demand for various applications. In addition, cobalt, commonly contained in cathodes ($LiCoO_2$) of LIBs, is partly mined in politically unstable countries [4]. Thus, new rechargeable battery systems are required, which can be made from environmentally friendly and earth abundant materials. Since sodium is the most abundant metal, non-toxic and lower cost, researchers are trying to replicate the performance of well-established LIBs with sodium based batteries. Due to the natural abundancy (ratio of reserves Li:Na = 1:1000), relatively lower cost (see Table 1) and very suitable redox potential ($E^o_{Na^+/Na} = -2.71$ V vs SHE, only 0.3 V above that of lithium) of sodium, rechargeable sodium-ion batteries (SIBs) would be a viable alternative to expensive lithium ion batteries [2,5,6]. Table 1 also compares chemical and electrochemical characteristics of lithium and sodium along with their chemical abundance. Substantial research, development, and demonstration efforts are currently in progress to develop Na^+ ion conducting electrolytes and compatible electrode materials for practically viable SIBs. SIBs are especially suitable for stationary applications where energy density is not very critical for large-scale energy storage with intermittent renewable energies such as solar, wind and tidal.

Although SIBs are more viable for stationary applications, GE global research center has identified sodium nickel technology for powering locomotives, mining trucks, tugboats and so on [7].

If the production of SIBs can be made practically possible, there will be much relief on the constraints of reserves, as well as relief on the cost and the environmental impact [2]. Conceptually, the possibility of these SIBs has been proved several years ago [8], but the topic has re-emerged very recently with the necessity to look for alternatives to lithium systems. Although, there are some SIBs in the market with reasonable energy densities, such as Na–S and $Na-NiCl_2$ (ZEBRA – Zero Emission Battery Research Activities) batteries, these require high temperature (~300 °C) for their proper operation due to the use of ceramic electrolyte $NaAl_{11}O_{17}$ (β-alumina) [3,5,9,10]. The main issue of present day research efforts relies on developing suitable electrolytes and electrode materials for room temperature SIBs. To fabricate room temperature rechargeable SIBs, electrolytes with reasonably high Na^+ ion conductivity and the ability to form better electrode–electrolyte interface are indispensable. A critical review on the progress of electrode materials, binders, additives and Solid Electrolyte Interface formation for SIBs has recently been published by Sawicki et al. [11]. They have also briefly discussed about the organic and ionic liquid based electrolytes and concluded that the prospects for SIBs as post-LIBs remain high since the cost, safety, cycling stability and energy density become more favorable. Several liquid (non-aqueous, aqueous and ionic), polymer gel and solid (ceramics, glasses, solid polymers and hybrid) electrolytes have been developed and evaluated at room temperature in the recent past. A bibliometric analysis of the publications on various types of electrolytes using the Web of Science was carried out to search through titles, abstracts or keywords since 1990. The number of publications in the past 25 years (see Fig. 1) clearly reveals that there is a significant and unprecedented growth of research around the world on electrolytes for SIBs. The major objective of this review is to highlight and discuss the present status of all different types of electrolytes and their physicochemical properties such as ionic conductivity, thermal properties (T_g and T_m), electrochemical stability, thermal stability and viscosity (see Table 2).

Table 1 – Comparison of lithium and sodium towards battery applications [2].

	Lithium	Sodium
Ratio of reserves	1	1000
Cost (for carbonate) (\$ ton^{-1})	5000	150
Atomic weight (g mol^{-1})	6.9	23
Ionic volume ($Å^3$)	1.84	4.44
Theoretical capacity (mAh g^{-1})	3829	1165
Normal electrode potential vs SHE (V)	−3.045	−2.714
Distribution (*)	70% in South America	Everywhere

*2013 review – room temperature stationary sodium ion batteries – energy and environmental science.

Electrolytes

Electrolyte is a medium responsible for ionic transport, typically for Na^+ ion transport in SIBs and hence controls the power density. Ionic conductivity is the topmost important property for an electrolyte and at the same time it should have negligible electronic conductivity in order to avoid short circuits. Electrolytes should also have good mechanical, electrochemical, thermal and voltage stability along with good interfacial properties. Thermal and voltage stability ranges of batteries will depend on the Lowest Unoccupied Molecular Orbital (LUMO) and Highest Occupied Molecular Orbital (HOMO) energy levels of the electrolyte as shown in Fig. 2 [8]. To have better thermal stability, redox energies E_a (anode) and

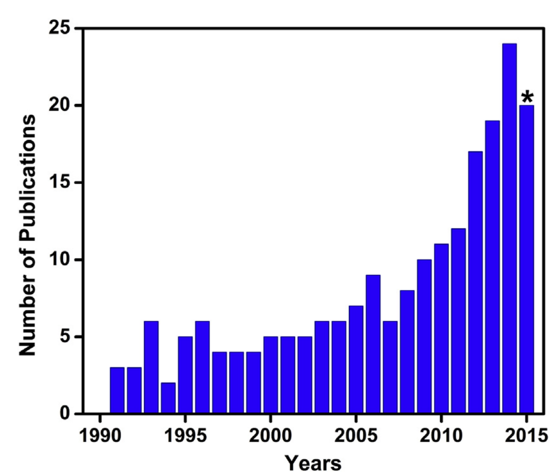

Fig. 1 – Number of publications on electrolytes for sodium ion batteries operating up to maximum temperature of 350 °C. *Publications up to October 2015.

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