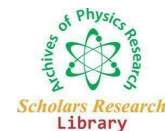




Extended Abstract

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CODEN (USA): APRRC7**Rechargeable batteries based on chloride ion transfer****Xiangyu Zhao***Nanjing Tech University, China**E-mail: xiangyu.zhao@njtech.edu.cn*

Alternative battery chemistries beyond lithium ion and using abundant electrode materials have been developed. Chloride ion battery (CIB) is a new rechargeable battery based on Cl⁻ anion transfer. This battery shows a variety of electrochemical couples with theoretical energy densities up to 2500 Wh l⁻¹, which is superior to those of conventional lithium ion batteries. Abundant material resources such as Mg, Ca, Na and metal chlorides (e.g., FeCl₃, CuCl₂ and MgCl₂) can be sustainable electrode candidates. The CIB includes a metal chloride/metal electrochemical couple and an ionic liquid electrolyte allowing chloride ion transfer, as reported in the proof-of-principle study of CIB operated at room temperature. The problem is that the metal chloride cathode can react with chloride ions in the electrolyte, leading to the formation of soluble complex anion. This electrode dissolution and the subsequent shuttle would limit the use of metal chloride cathode in the liquid electrolyte system. Metal oxychlorides with higher stability have been proved to be new cathode materials for CIBs. Metal oxychloride/metal systems could also show high theoretical energy densities during the chloride ion transfer. By carbon incorporation in the cathode or optimization of electrolyte composition, more than 70% of the theoretical discharge capacity of single-electron cathode such as FeOCl or VOCl could be delivered. A preliminary study on the multi-electron VOCl₂ cathode was also reported in the electrode system using VOCl as cathode and Mg/MgCl₂ composite as anode. Besides inorganic electrode materials in rechargeable batteries, organic electrode materials, in particular polymers, have been attracting much attention, due to their advantages of good electrochemical performance, high stability, abundant chemical elements, structural tunability and designing flexibility. Chloride ion doped polymer materials have been studied and developed as new cathodes for chloride ion batteries. Reversible redox reactions and superior cycling stability were obtained. The Chloride Ion Battery is conceptually similar to the Fluoride Ion Battery, just that the Cl⁻ replaces the fluoride ion. A series of metal chloride/metal combinations demonstrate theoretical energy densities above those of the current LIBs which makes them attractive. The evident advantage of this battery system lies in the fact that active material electrodes can be built from abundant material resources and it is possible to use various metals such as Li, Na, Mg, Ca, and Ce, as well as their corresponding chlorides. The CIB includes a metal chloride/metal electrode system and an ionic liquid electrolyte allowing chloride ion transfer, as reported in the proof-of-principle study of CIB operated at room temperature. 1 The problem is that the metal chloride cathode can react with chloride ions in the electrolyte by a Lewis acid/base reaction, leading to the formation of soluble complex anion (e.g., FeCl₄⁻ and CuCl₄²⁻), which could be electrochemically reduced to metal. This electrode dissolution and the subsequent shuttle would limit the use of metal chloride cathode in the liquid electrolyte system (see Figure S1). Metal oxychlorides with higher stability have been reported as new cathode materials for CIBs.

The chloride ion battery has been developed as one of the alternative battery chemistries beyond lithium ion, toward abundant material resources and high energy density. Its application, however, is limited by the dissolution of electrode materials and side reactions in the liquid electrolyte. Herein, a solid polymer electrolyte allowing chloride ion transfer and consisting of poly(ethylene oxide) as the polymer matrix, tributylmethylammonium chloride as the chloride salt, and succinonitrile as the solid plasticizer is reported. The as-prepared polymer electrolyte shows conductivities of 10⁻⁵–10⁻⁴ S cm⁻¹ in the temperature range of 298–343 K. When it is assembled with the iron oxychloride/lithium electrode system, reversible electrochemical redox reactions of FeOCl/FeO at the cathode side and Li/LiCl at the anode side are realized, demonstrating the first all-solid-state rechargeable chloride ion battery. A novel room temperature rechargeable battery with VOCl cathode, lithium anode, and chloride ion transporting liquid electrolyte is described. The cell is based on the reversible transfer of chloride ions between the two electrodes. The VOCl cathode delivered an initial discharge capacity of 189 mAh g⁻¹. A reversible capacity of 113 mAh g⁻¹ was retained even after 100 cycles when cycled at a high current density of 522 mA g⁻¹. Such high cycling stability was achieved in chloride ion batteries for the first time, demonstrating the practicality of the system beyond a proof of concept model. The electrochemical reaction mechanism of the VOCl electrode in the chloride ion cell was investigated in detail by ex situ X-ray diffraction (XRD), infrared spectroscopy (FTIR), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). The results confirm reversible deintercalation–intercalation of chloride ions in the VOCl electrode.

Bottom Note: This work is partly presented at *3rd International Conference on Electrochemistry* July 10-11, 2017, Berlin, Germany