INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 41 (2016) 6954–6964

Available online at www.sciencedirect.com

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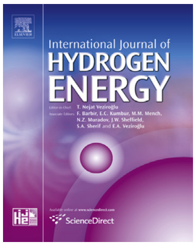

High stable Li-air battery cells by using PEO and PVDF additives in the TEGDME/$LiPF_6$ electrolytes

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ARTICLE INFO

Article history:
Received 4 May 2015
Received in revised form
2 November 2015
Accepted 12 November 2015
Available online 22 December 2015

Keywords:
Li-air battery
Cycle life
Stability
TEGDME
Organic additives

ABSTRACT

An ether based electrolyte containing TEGDME/$LiPF_6$ was optimized, which possessed low viscosity and high ionic conductivity, under dry argon atmosphere in a glove box. In order to prevent air breathing cathode clogging by lithium oxide and provide stability of Li metal anode, different types in varying quantities of polymeric additives such as PEO and PVDF were added into TEGDME/$LiPF_6$. These additives are thought to promote the dissolution of lithium peroxide precipitates formed in course of discharge process and protect the anode. Graphene/α-MnO_2 nanocomposite air breathing structure coated on nickel mesh was used as cathode. A lithium disk was used as anode while glass fiber was used as the separator in ECC-Air test cells. The cells were cyclically tested using 0.1 mA/cm^2 current density over a voltage range of 2.15–4.25 V. Electrochemical impedance spectroscopy (EIS) measurements was applied to investigate the effect of the polymeric additives on the resistivity of the electrolyte. Results revealed that polymer contained electrolyte structures with PVDF addition provided not only good discharge capacity but also excellent stability. After the electrochemical cycling test, the morphologies of the cathodes were analyzed using scanning electron microscopy (SEM), X-ray diffraction (XRD) analysis, and Raman spectroscopy to determine the reaction products.

Introduction

Demand for better electric vehicles motivates the search for lower cost and higher specific capacity rechargeable batteries. Recent developments in battery technology have been driven by the need for high energy density batteries suitable for automotive applications. In recent years the Li-air batteries has received a considerable amount of attention as the theoretical specific energy density is equivalent to that of gasoline [1]. The reversible Li-air battery has the potential to revolutionize energy storage for hybrid and electric vehicles. The high theoretical specific energy density is associated with Li_2O_2 formation upon discharge with a non-aqueous electrolyte [2].

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http://dx.doi.org/10.1016/j.ijhydene.2015.11.061

Aprotic electrolyte Li-air batteries have received considerable attention due to very high theoretical specific energy, but degradation during cycling of every major component of the O_2 electrode, including solvent, lithium salt, binder and carbon, has plagued efforts to develop this technology for practical purposes [3–5]. Developing stable electrolyte for the rechargeable aprotic Li–O_2 cells has been considered as one of the biggest challenges [6,7].

The development of non-aqueous Li-air or Li–O_2 batteries presents a number of challenges, such as selection of an efficient and stable electrolyte, decrease of charge–discharge voltage hysteresis, design of catalysts and substrate materials to achieve high capacity and stability, protection of Li anode and supply of moisture-free air. The desired electrolyte should be chemically and electrochemically stable in a wide potential range in the presence of oxygen and its reduced species and have high oxygen solubility, high ionic conductivity, adequate wettability to cathode, and low volatility [8].

There has been recent experimental and theoretical evidence that the organic carbonates (e.g. propylene carbonate, ethylene carbonate, and dimethyl carbonate) commonly used in Li-ion batteries are not stable against oxygen reduction reaction during discharge [3,4]. Therefore, conventional Li-ion battery electrolytes, such as those based on organic carbonate solutions used in the initial development of Li-air batteries, are not appropriate. In particular one development is that an organic solvent can survive nucleophilic attack of the superoxide radical (O^{2-}), an intermediate phase formed from the oxygen reduction reaction upon discharge [7–11]. Neither Li_2O_2 nor Li_2O are major components of the insoluble discharge products; instead, the products are mainly Li_2CO_3 and others resulting from the decomposition of carbonate electrolytes. Li_2CO_3 is not electrochemically reversible in an aprotic lithium–air battery system, which will limit their chargeability, cycle life and stability in lithium–air batteries [2,12].

Room temperature ionic liquids (RTILs), largely employed in lithium ion batteries have also been proposed as suitable electrolyte for Li–O_2 cells due to their high conductivity, non-volatility, non-flammability and wide temperature range of operations. It has been reported that RTILs exert a beneficial action on the kinetics at the cathode of a Li-air cell and this behavior was attributed to the build-up of a less resistive film at the cathode/air/electrolyte interface as well as to improve Li_2O_2 solubility in the RTIL, leading to a reduced Li_2O_2 particles size. Ethers and glymes are considered good candidates as solvents for the non-aqueous Li–O_2 battery as they may have a fairly low vapor pressure. Ether based electrolytes such as tetraethylene glycol dimethyl ether (TEGDME) is reported another important direction for aprotic type lithium-air batteries. Compared with the carbonate electrolytes, ether electrolytes have better stability in the process of charge and discharge [13]. TEGDME has a room temperature vapor pressure of approximately 10^{-5} bar [5]. It is reported that the hydrophobicity of some RTIL in the lithium-air cell and considered TEGDME as a suitable electrolyte component due to their capability to prevent the vaporization of electrolyte and hydrolysis of anode [14–16]. Due to their unique physicochemical properties, these "designer solvents" have been intensively investigated for various applications [17,18]. Ionic liquids are therefore promising electrolytes for rechargeable lithium–air batteries, and the selection of an electrolyte stable to both the Li and oxygen electrode is recognized as a major future direction of research [19].

Ether-based solvent of TEGDME (or tetraglyme) have attracted significant attention for the Li–O_2 battery very recently, mainly due to the relatively high stability with respect to superoxide radicals and oxidation potentials (>4.5 V versus Li/Li^+), inflammability, high thermal stability, and low cost [6,20]. In this study, the effects of polymeric additives on TEGDME/$LiPF_6$ electrolyte on the performance of lithium-air batteries were aimed to investigate. In this work, we examine the effects of electrolyte composition on the capacity and cycling ability in the TEGDME/$LiPF_6$ based polymer reinforced electrolytes. PVDF and PEO additives showed that TEGDME/$LiPF_6$ cycleability exhibited remarkably high cycle life with small quantity of polymers.

Experimental

Electrolyte preparation and Li–O_2 cell assembly

Electrolytes with 1 M prepared in a dry argon atmosphere in a glove box (MBRAUN LABstar). Electrolyte was produced by dissolution of the powder $LiPF_6$ (98 +%, Alfa Aesar) salt in TEGDME (≥99% Sigma–Aldrich) (1 M solution of $LiPF_6$ salt in TEGDME). In the first step, PEO (Alfa Aesar) and PVDF were dissolved separately in TEGDME for 2 h. After this process, $LiPF_6$ was added into the solution and stirred for a day.

Graphene and of 30 wt. % α-MnO_2 nanowire added nanocomposite was used as air breathing cathode material. The detail of synthesizing of α-MnO_2 nanowires was in our previous work [21]. Graphene/30 wt. % α-MnO_2 mixtures were coated on the nickel mesh by doctor blade with a 2.54 cm^2 cathode surface area. A lithium disk (2.01 mm^2) was used as anode while glass fiber (18 mm, ECC1-01-0012-A/L) was used as the separator in Li–O_2 cell. Before the air cell assembling, both the separator and the cathode were dried overnight at 50 °C. The Li–O_2 cell was then assembled in glove box using an ECC-Air electrochemical cell (EL-Cell, GmbH) configuration with allowing oxygen to enter and exit through the cathode side. The cells were aged for 10 h of rest at open circuit potential (OCV) before measurements.

Structural and electrochemical characterization

The microstructure of the air breathing electrode was analyzed using SEM (JSM-6060 LV system). The phase structures of the deposited films after discharging process on the air breathing cathodes were investigated by XRD (Rigaku D/MAX 2000 with thin film attachment) with CuKα radiation. Raman spectroscopy analyze of the air breathing cathodes was performed by Kaiser RAMANRXN1 for further investigation of the phase composition after cycling. The Raman scattering spectra of products were recorded using 785 nm invictus laser light source with a low excitation power of 5 mW. The cyclic voltammetry (CV) was performed on Gamry Reference 3000 workstation. CV was carried out at a scan rate of 0.5 mV^{-1} in a potential range from 2.15 to 4.25 V in the Li–O_2