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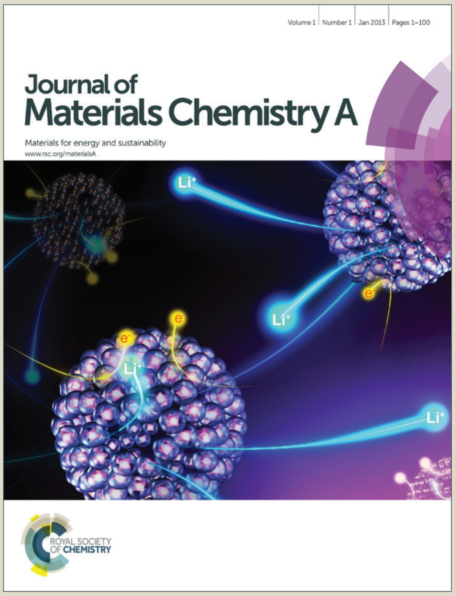

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An aqueous electrolyte rechargeable Li-ion/polysulfide battery

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Abstract

In spite of the great efforts of battery communities on Li-S batteries in aprotic organic electrolytes, there have been very few studies showing the potential application of this system in aqueous electrolyte. Herein, we explore this option and report on a cheaper and safer new aqueous system coupling a well-known cathode material in Li-ion batteries (i.e. $LiMn_2O_4$) with a dissolved polysulfide anode. In comparison with classical Li-S batteries containing aprotic organic solvents, the aqueous electrolyte offers a stable cycling profile over 100 cycles with faster C-regime.

Key Words: Aqueous electrolyte, polysulfide, $LiMn_2O_4$, Li-S batteries, energy storage

1. Introduction

Technological and societal demands for higher capacity and cost effective energy storage options provide an impetus for the exploration of alternative electrochemical energy storage systems. Over the past 20 years, lithium ion batteries (LIBs) have played a crucial role in the development of such energy storage technologies[1]. Although great improvements have been accomplished and active research toward further developments continues, current lithium-ion technologies provide a limited gravimetric energy density.

Use of earth abundant sulfur provides a promising alternative for achieving high-energy and low-cost battery systems. For instance, non-aqueous electrolyte based lithium-sulfur (Li-S) batteries offer a five-fold increase in energy density compared with the present Li-ion technologies[2,3,4]. Li-S batteries represent a valuable option as they combine a variety of desirable traits, including low equivalent weight, high capacity (1675 mAh/g), low cost, and environmentally benignancy. All these characteristics cannot be accomplished with current Li-ion technology. However, Li-S battery technology faces several drawbacks that lead to poor cycle life, which has prevented its practical realization until recently. Besides the insulating nature of sulfur, which thus requires close contact with a conductive matrix (namely porous carbon), another big challenge in Li-S batteries is the formation of non-soluble and insulating reduced sulfur species (Li_2S). Upon cycling, Li_2S precipitates on the composite matrix as nonconductive slabs, resulting in poor electrical contact[5,6]. Recently, dissolved polysulfide (so called catholyte) rather than sulfur impregnated composites has been used to further eliminate the formation of Li_2S within the porous structure and leads to a superior performance compared to conventional Li–S cells[5]. Even though such an improvement holds great promises, the SEI layer formed on Li and the resulting effects are not fully understood. Thus, finding safe and low cost energy storage systems remains a challenge.

Aqueous rechargeable batteries offer an opportunity to fulfill those criteria through the use of non-combustible aqueous electrolytes. Aqueous electrolytes have many advantageous over organic counterparts. Water is cheaper than organic solvents, and cost effective salts and separators are available. Since the ionic conductivity of aqueous electrolytes are about two orders of magnitude higher than organic electrolytes[7], they ensure higher rate capabilities well above the classical cycling rate obtained from state-of-the-art Li-ion or Li-S batteries[1].

Despite many advantages of aqueous electrolytes, water suffers from its low thermodynamic stability window (1.23 V), resulting in lower energy density than for instance current Li-ion batteries. The stability window of water shifts with pH, specifically 0.059 V per pH unit, as can be seen from the Pourbaix diagram (Fig. 1). Fortunately, in some practical applications the value is well above its thermodynamic limits as it is known from Pb-acid technology (between 2.0-2.15 V) due to the high hydrogen overpotential of Pb as well as electronically insulating but ionically conductive $PbSO_4$, across which there is a steep potential gradient[8].

Aiming to gain the advantages of both Li-ion and Li-S technologies, herein, we propose to use an aqueous electrolyte rechargeable polysulfide battery system in combination with commercial lithium battery electrode materials whose performances in aqueous media are already well-known[9]. The benefit of this aqueous electrolyte Li-ion/polysulfide system will be twofold, combining the higher C-regime capabilities of Li-ion technologies with the enormous polysulfide solubility and long cycling performances of Li-S technologies.

The redox reaction of aqueous polysulfides is different from the reaction in organic electrolytes. In organic electrolytes the sulfur generates a range of polysulfides (Li_2S_x, $2<x<8$) during reduction leading to insoluble and insulating Li_2S. The reduction phenomenon differs in aqueous electrolyte in which three main chemical species are formed, $H_2S(aq)$, HS^-, and S_x^{2-}, determined by the pH. Thus, an over-simplified reaction mechanism can be written as in (Eq. 1)[10-12] where the average voltage lies approximately at -0.5 V vs SHE corresponding to 2.5 V vs Li. Additionally, the high capacity and rates result from the anomalously high solubility of polysulfide salts in water, contrary to non-aqueous electrolytes in which for instance Li_2S is not soluble.

$$S_2^{2-} + 2H_2O + 2e^- \leftrightarrow 2HS^- + 2OH^- \quad E_o = -0.51 \text{ V vs SHE} \qquad \text{(Eq. 1)}$$

The use of polysulfides in aqueous electrolytes were suggested by Licth *et al.* and co-workers more than 20 years ago either in batteries or in photoelectrochemical solar cells[10-13]. Afterwards, this topic falls into oblivion until it was recently revisited by Visco *et al.*[14] In their patented work, the authors demonstrated the feasibility of using aqueous electrolyte Li-S batteries provided the use of a high cost Li-ion conductive glass membrane as Li anode protective layer. Moreover, the capacity of sulfur would not be maximized with the proposed aqueous electrolyte Li-S batteries due to the critical instability of water (Fig. 1); the cut-off voltage will thus be limited to 2.2-2.3 V vs Li (depending on the pH value) affording only one fourth of the entire theoretical capacity (1675 mAh/g).

Therefore, our first approach depicted here is based on the use of a Li-ion/polysulfide cell configuration that might be able to replace the expensive membrane with cost-effective cationic membranes for a cheap, sustainable and high power storage device. The choice of dissolved polysulfide rather than sulfur/carbon composites[15] aims to increase the energy density by high solubility of polysulfide in water which is not the case for elemental sulfur. As a prototype example, dissolved polysulfide in combination with $LiMn_2O_4$ will be presented. The combination of $LiMn_2O_4$ together with polysulfide is within the stability window of water, thus, the reduction and oxidation of water does not crucially influence the lithium transport kinetics of the electrodes ensuring a safe and reliable working condition (Fig. 1).

2. Experimental

Materials and Electrode Preparations: $LiMn_2O_4$ is received from Sigma Aldrich and used as it is without further treatment. Working electrode (WE) for CV measurement were prepared by mixing $LiMn_2O_4$ powders with Ketjen-black carbon and an organic binder (PVDF), in a weight ratio of 80:10:10 in NMP (n-methyl pyrrolidone), both also from Sigma-Aldrich. After stirring, the mixture was casted on a 316 SS grade stainless steel electrode then dried at 100 ^oC for 5 h.

For the preparation of aqueous polysulfide solution, potassium (poly)sulfide (>42 % K_2S) was purchased from Sigma-Aldrich. HPLC grade water was employed in the experimennts which was not deoxygenated prior to use. First a 18 mL 0.5 M Li_2SO_4 containing electrolyte was prepared in a beaker cell then around 1.2 g potassium (poly)sulfide was dissolved into the electrolyte.

For the preparation of the galvanic cell, first 18 mL, 0.5 M Li_2SO_4 containing electrolyte was prepared into two beaker cell; one for the $LiMn_2O_4$ and the other for the dissolved polysulfide part. Then the cells were sealed and separated from a salt bridge in which $LiMn_2O_4$ is used as WE, dissolved polysulfide as counter electrode (CE) and SCE as reference (RE). $LiMn_2O_4$ was dipped into the galvanic cell in which the electrode area was about 2.5 cm^2, and the weight of active material was typically in the range of 7–10 mg for each sample.

For the full cell configuration, a home-made and modified 2-electrode Swagelok Teflon cell was used (Fig. 5a inserted picture). First $LiMn_2O_4$ containing slurry (as depicted above) was prepared, casted on a stainless steel disk electrode and dried at 100 ^oC for 5 h that was used as

WE. The electrode area was 0.9 cm^2, and the weight of active material was typically in the range of 2–3 mg for each sample. As a CE, 0.2 ml aqueous polysulfide solution was used together with 5mg Ketjen black carbon powder as conductive additives as. As a separator, a lithium ion conducting glass ceramic (LIC-GC) consisting of Li_2O-Al_2O_3-SiO_2-P_2O_5-TiO_2-GeO_2, which was supplied from Ohara Inc., Japan, was used.

Electrochemistry: All potentials will be reported here vs. the standard calomel electrode (SCE). Electrochemical characterization was performed by the use of both cyclic voltammetry (CV) and galvanostatic cycling with potential limitation (GCPL) using VMP-3 instrument from Biologic with 0.5 M Li_2SO_4 aqueous electrolyte inside a beaker cell. CV measurements were performed with a 3-electrode cell configuration. For $LiMn_2O_4$ test; a scan rate of 0.2 mV/s over 0.4-1.2 V vs SCE was applied in which carbon coated stainless steel was used as CE, SCE as RE and $LiMn_2O_4$ as WE. For the dissolved polysulfide CV test; a scan rate of 5 mV/s over -1.0 to 0.3 V (vs SCE) was applied in which carbon coated stainless steel was used as WE and SCE as reference electrode.

For the Galvanic cell test, $LiMn_2O_4$ was used as WE and separated by a salt bride from the CE polysulfide containing aqueous electrolyte cell. SCE was used as RE and a current density of C/100 with the voltage values ranging from 0.2 to 1.0 V was applied using VMP3 galvanostat/potentiostat.

For the full cell configuration, experiments were carried out using two-electrode modified Swagelok-type cells. The electrolyte consisted of a solution of 0.5 M of Li_2SO_4 in water. A current density of C/2 with the voltage values ranging from 0.2 to 1.7 V using galvanostat/potentiostat VMP3 was applied. SCE reference electrode was placed into the $LiMn_2O_4$ cell.

3. Results and Discussion

To show the electrochemical activity of $LiMn_2O_4$ and polysulfide, cyclic voltammetry (CV) studies were performed in a 0.5 M Li_2SO_4 containing aqueous electrolyte. Fig. 2a shows the two reversible redox couples at the scan rate of 0.2 mV/s, that are situated at 0.68/0.76 and 0.82/0.90 V (vs SCE), respectively, corresponding to the two-step intercalation/deintercalation of Li^+ into/from $LiMn_2O_4$, which is already well studied in aqueous electrolytes[9,16,17]. CV of the dissolved polysulfide at the scan rate of 5 mV/s are shown at Fig. 2b with one redox couple whose peak appeared at -0.3/-0.8 V (vs SCE) which is due to the electrochemical signal of polysulfide in water[10,14].

The electrochemical performance of sulfur (or its reduced polysulfide species) in aqueous media has a totally different signature from non-aqueous solutions. Sulfur reduction in non-aqueous electrolytes takes places via transformation of long-chain polysulfides to short-chain polysulfides, and is accompanied with visible color changes that have been studied by UV-vis spectroscopy measurements[18] (i.e. long-chain polysulfides adsorb light at higher wavelengths compared to the short chain polysulfides and the reversible color changes of the electrolyte from reddish to yellowish during sulfur reduction and vice versa during oxidation was detected). However, what we observe here is that no reversible color change occurs upon cycling of dissolved polysulfides in aqueous media. The color transforms from dark orange to greenish, and even disappears if the cells are not properly sealed (Fig. 3). This color change can be further monitored with pH measurements. While the pH of starting polysulfide was 12.1, it is reduced to 9.2 at the end of the cycling. Since it is known that the bisulfide ion (HS^-) is the primary species in the pH range of natural waters, while the hydrogen sulfide molecule (H_2S(aq)) becomes the predominant reduced sulfur species below pH 7[19], we believe that the color alteration accompanied by pH changes can be correlated with the generation of gaseous discharge product of sulfur (HS^- or H_2S(aq)). Thus, depending on the type of cells and how they are sealed, cycling performances may differ.

Prior to assembling a full cell configuration, three-electrode galvanostatic cycling measurements were performed with a galvanic cell design in order to investigate the behavior of each half-cell. For this purpose, two cell compartments were prepared individually and separated by a salt bridge (Fig. 4a) where $LiMn_2O_4$ was employed as working electrode, carbon coated stainless steel electrode immersed into a dissolved polysulfide containing aqueous electrolyte as counter electrode, and SCE as reference electrode. Due to the huge resistance resulting from the salt bride, C/100 cycling regime (which corresponds to the current required to completely charge/discharge an electrode in 100 hours) was applied. Fig. 4b shows the half-cell of $LiMn_2O_4$ cycled between 0.2 – 1.0 V (vs SCE), corresponding to 3.44– 4.24 V (vs Li), which presents two distinct voltage plateaus at 0.75 and 0.85 V (vs SCE). During the cycling of $LiMn_2O_4$, we also monitored the changes of the counter electrode cell potential containing dissolved polysulfide as can be seen in Fig. 4b. The oxidation and thereafter reduction of $LiMn_2O_4$ was compensated by the reduction and oxidation of the polysulfide, respectively. The cell voltage remained at -0.55 V (vs SCE), which was already confirmed by the CV measurement as depicted above in Fig. 2b, belonging to the electrochemical signal of polysulfide species in aqueous electrolyte. Keeping in mind that the cell was not balanced and excess of polysulfide were used here ensuring to compensate the elimination of gaseous active material in the cell. Otherwise, we faced to have a problem of the depletion of the generated gaseous (i.e. H_2S) from the cell resulting color disappearances (Figure 4a). Accordingly, instead of the cycling behavior of the polysulfide species, the signal from the oxidation of water was detected at 0.6 V (vs SCE) due to the lack of active material during 3-electrode measurement (Fig. S1). As explained, when the cells are not sealed properly, a visible color vanishing along with reduction of the pH was detected.

The galvanostatic discharge-charge profile of the full cell ($LiMn_2O_4$ with polysulfide in the presence of 0.5 M Li_2SO_4 containing aqueous electrolyte) at C/2 rate is shown at Fig. 5a. The active materials were separated by a Li-ion conducting glass membrane (LIC-GC), which was already used in the field of lithium batteries[20], and a modified Swagelok type cell was used for the measurements (Fig. 5a inserted picture). As a whole, an average 1.5 V cell voltage is obtained with $LiMn_2O_4$/polysulfide redox couple. Although the cell voltage is less than the classical Li-S batteries whose voltages lie at an average of approximately 2.2 V, the lower potential is not detrimental and is compensated by a lower initial cost and higher power density provided by the aqueous electrolyte. Last but not least, the common fast capacity decay phenomenon seen in classical Li-S batteries was not observed with the present Li-ion/polysulfide system, resulting in superior cycling retention over 100 cycles (Fig. 4b).

4. Conclusions

Here, we demonstrated a proof of concept for a Li-ion/polysulfide system as a cheaper and higher power option to either conventional Li-S batteries or current vanadium flow and lead acid batteries. $LiMn_2O_4$, a well-known cathode material studied in aqueous media for many years, was chosen as positive electrode without further optimization. The electrochemical characterization of the dissolved polysulfide was studied by means of CV and galvavostatic cycling showing its one redox couple whose average voltage lies at -0.55 V vs SCE. From a safety point of view, special care needs to be taken into account since generated gaseous compounds (i.e. H_2S) might escape from the cell compartment. This removal of the active material was confirmed by monitoring the pH whose value was found to drop from 12.1 to 9.2 upon cycling along with a visible color disappearance. A 1.5 V cell voltage and 110 mAh/g capacity is obtained with almost no fading over 100 cycles which is superior to classical Li-S cells. Moreover, higher conductivity of the aqueous electrolyte as well as faster charge-transfer kinetics in aqueous rechargeable lithium cells are the main advantages over non-aqueous electrolytes.

For the future, the distribution of reduced sulfur species will be investigated via a carefully controlled study of the pH. Moreover, a survey of different electrolyte additives able to trigger polysulfide chemical reactions and kinetic behavior in aqueous electrolyte will be studied together with the tailor-made Li-ion cathode materials leading to a full cell configuration with higher energy density. Additionally, Li will be replaced by Na allowing much cheaper option for the current system.

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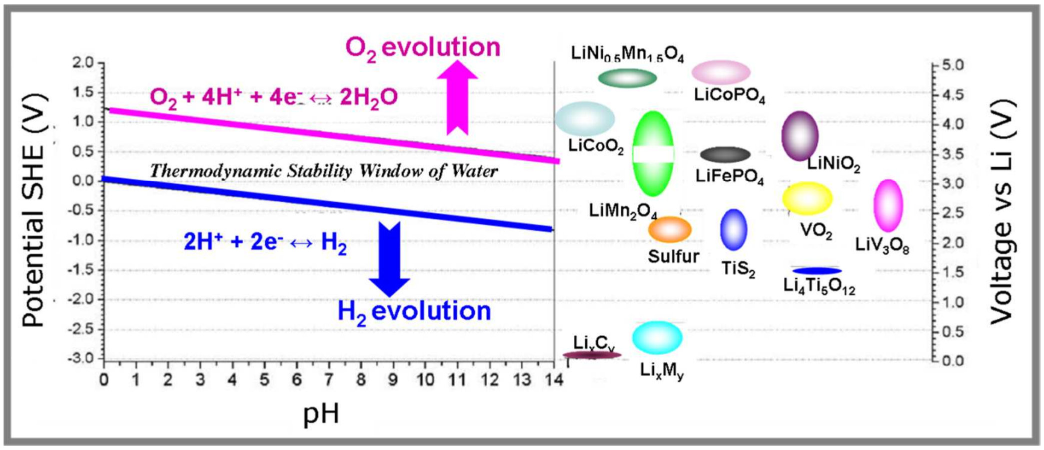

Fig. 1 Thermodynamic stability window of water together with the several electrode materials in lithium-ion batteries[9]

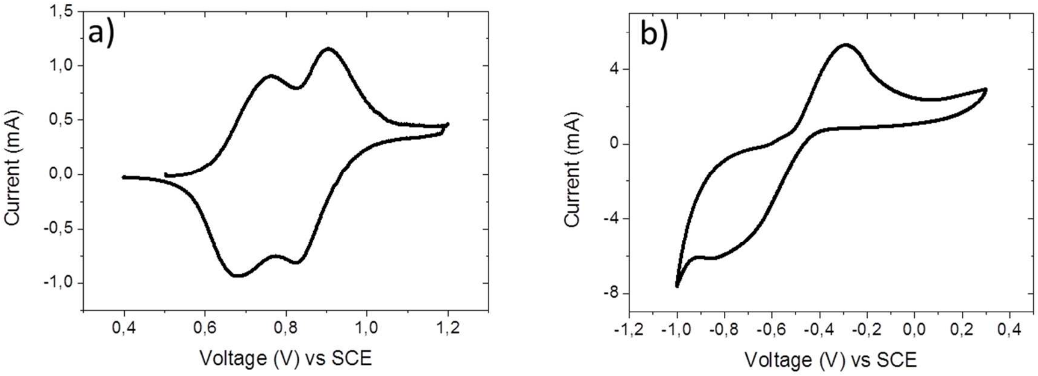

Fig. 2 a) Cyclic voltammograms for $LiMn_2O_4$ at the scan rate of 0.2 mV/s over 0.4-1.2 V vs SCE b) cyclic voltammograms of dissolved polysulfide at the scan rate of 5 mV/s over -1.0 to 0.3V vs SCE

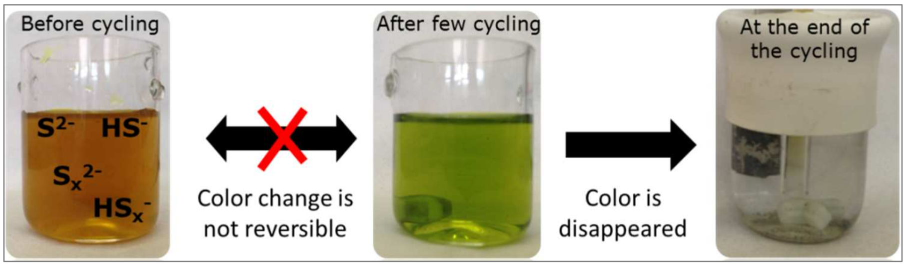

Fig. 3 The dissolved polysulfide in aqueous electrolyte showing the color change and color disappearances upon cycling

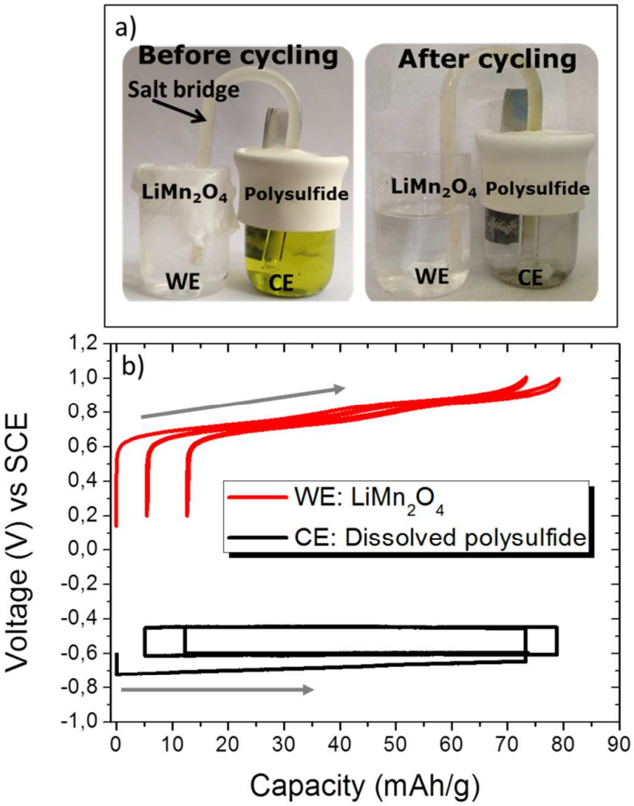

Fig. 4 a) A galvanic cell design used for the experiments in which $LiMn_2O_4$ is used as WE and dissolved polysulfide as CE, b) half-cell galvanostatic performance of $LiMn_2O_4$ (red) and dissolved polysulfide (black) at a current density of C/100

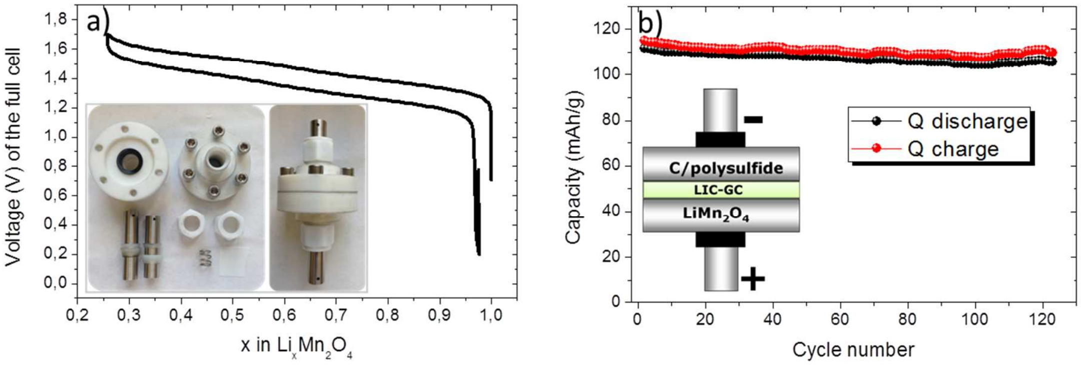

Fig. 5 a) First galvanostatic charge-discharge profile of the $LiMn_2O_4$/polysulfide full cell at a current density of C/2 for the voltage range between 0.2 and 1.7 V b) cycling performance of the cell in 0.5 M Li_2SO_4 contaning aqueous electrolyte