Exploring sulfur solubility in ionic liquids for the electrodeposition of sulfide films with their electrochemical reactivity toward lithium

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ABSTRACT

Metal binary sulfides (TiS_2, FeS_2), in either powder or thin film forms, were the first studied Li insertion electrodes for rechargeable lithium batteries, with thin films made mainly by sputtering. Here we exploit the equilibrium solubility of molecular sulfur into ionic liquids at its melting point ($120 °C$), which we estimated to be at a maximum level of 80 mM by both electrochemical and microwave studies, to prepare thin films of both Co_9S_8 and FeS_x showing initial capacities of 559 mAh g^{-1} and 708 mAh g^{-1} versus lithium in coin cells, respectively. We demonstrate that the growth of Co_9S_8 films involves the reaction of soluble sulfur with the electrodeposited Co metallic layer, while the formation of FeS_x films enlists a precipitation between the reduced Fe(II) cations and the electrochemically produced $S_x{}^{y-}$ species in the ionic liquid bath. Such findings, namely the solubility of sulfur into ionic liquids, open opportunities to electrodeposit sulfur-based compounds as well as capture sulfur from various media enabling a better environment.

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1. Introduction

During the past few decades, transition metal chalcogenides have been, and still are of great interest for energy storage applications (e.g. batteries) because they display a full array of attractive physical and chemical properties [1–5]. TiS_2 was, for instance, the first studied insertion electrode for rechargeable Li batteries [6] while iron sulfide has long been recognized for its possible use as electro-catalyst for hydrogen evolution and oxygen reduction [7]. Primary Li batteries based on FeS_2 positive electrodes and photovoltaic cells based on active CuS layers are presently commercialized [8–10]. Aside from the aforementioned sulfides, cobalt sulfides have also attracted the attention of researchers dealing with the fields of supercapacitors, magnetic, fluorescent, catalysts and dye-sensitized solar cells [11]. The arrival of conversion reactions has rekindled the interest for metal sulfides with respect to the field of lithium batteries. The benefit of these conversion reactions (ex: $CoS + 2Li^+ + 2e^- \rightarrow Li_2S + Co$)[12–14] is the impressive capacity gain that they can provide owing to the fact that they are not limited to 1e$^-$ per 3d-metal as for classical Li insertion/deinsertion reactions but can involve up to 3 or 4e$^-$ per 3d-metal. Hence our desire to prepare a few sulfides (Co_xS_y and Fe_xS_y) to determine the benefits that metal sulfide thin film electrodes could present.

There are several structural forms of cobalt sulfides: cubic Co_4S_3, hexagonal CoS, cubic Co_9S_8, and others which can be prepared as hollow nanocrystallites [15], submicron fibers [16], thin amorphous or crystalline films [17,18] and micrometric/submicrometric powders with different morphologies. In contrast, iron disulfide occurs naturally in two forms: pyrite and marcasite. It is found in both the most ancient magnetic rocks and more recent sedimentary deposits [19].

A variety of methods has been used for the growth of sulfide thin films, and it includes chemical-vapor deposition (CVD), sputtering, spray pyrolysis, evaporation, molecular beam deposition, and so on [20–24]. Aside these high temperature processes, the low temperature electrodeposition technique is low cost and highly versatile as it enables deposits of various materials on irregular surfaces, especially for the application in three-dimensional microbatteries [25]. Conventionally, three strategies have been used for the electrodeposition of metal sulfide thin films. They are (a) the anodic oxidation of the parent metals in sulfides containing electrolytes, (b) the cathodic co-reduction of metal ions and chalcogenide oxyanions on an inert substrate; and (c) the cathodic reduction of the metal ion from a non-aqueous solvent containing sulfur in elemental form, such as dimethylsulphoxide (DMSO), dimethylformamide(DMF) and ethylene glycol [26–29].

Ionic liquids are nowadays emerging as attractive media for electrodeposition because they enable to overcome the limits

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imposed by common aqueous or organic media. They offer a wide electrochemical window (up to 6V) and extremely low vapor pressures which allow deposition at temperatures well above 100 °C [30]. Such attractive characteristics have so far been widely exploited for the electrodeposition of metals and semiconductors [31–33] but barely used for the growth of binary oxides, except for ZnO [34,35], CeO$_2$ [36], NiO [37] and CdS [38], as far as we know. By exploiting the ability of ionic liquids to solubilize molecular sulfur at its melting point, we recently reported the electrodeposition of covellite CuS thin films with flakes morphology in an [EMIm] TFSI (1-ethyl-3-methylimidazolium bis (TriFluoromethaneSulfonyl)imide) electrolytic bath containing Cu(TFSI)$_2$ salt and elemental sulfur at 120 °C [39]. Herein we are further extending this approach to the synthesis of Co- and Fe-based sulfides.

As we are one of the pioneers in the growth of S-based compounds in ionic liquids basic science must be undertaken in order to determine the physical and chemical properties of sulfur in ionic liquid media, namely solubility, and establish the sulfur electrochemical reduction mechanism in ionic liquid, both of which are essential for mastering the growth of sulfide thin films in ionic liquid media. Common available literatures [40–44] on sulfur reduction reveal that, depending upon the solvents, the reaction can enlist different reaction pathways. For example, from cyclic voltammetric (CV) studies performed in dimethylsulfoxide (DMSO), Sawyer et al. [40] proposed that the first and second reduction peaks are associated with two consecutive two-electron processes: $S_8 + 2e \rightarrow S_8{}^{2-}$ and $S_8{}^{2-} + 2e \rightarrow S_8{}^{4-}$ respectively, with therefore the formed $S_8{}^{4-}$ specie being not stable as it dissociates into $S_4{}^{2-}$ according to the following reaction scheme: $S_8{}^{4-} \rightarrow 2S_4{}^{2-}$ or $S_8{}^{2-} \rightarrow S_6{}^{2-} + 1/4S_8$. With the renewed interest in Li-S batteries, the reduction of sulfur in various Li-based organic electrolytes has become a hot topic with very contradictory results [45–48]. Whatever the reacting media used, all the aforementioned studies commonly convey a complex sulfur reduction mechanism that should not be expected to be easier in ionic liquids; this is most likely the reason why it has not been investigated yet according to the best of our knowledge.

Within this context, the present manuscript is structured as follows. First the determination of the equilibrium solubility of sulfur in the ionic liquid [EMIm]TFSI (1-ethyl-3-methylimidazolium bis(TriFluoromethaneSulfonyl)imide) at 120 °C is presented, by focusing on the equilibrium between liquid sulfur and soluble sulfur in the bath. Then, the growth of cobalt and iron sulfide films in sulfur containing ionic liquid media, via electrodeposition is detailed and the electrochemical performances of the electrodeposited films in Li-batteries are presented. We found sulfur to be soluble in [EMIm]TFSI at a maximum level of 80 mM at 120 °C and demonstrated the feasibility of successfully growing, at such a temperature, Co$_9$S$_8$ and FeS$_x$ thin films showing large initial capacities which could not be maintained upon cycling.

2. Experimental

A closed electrochemical cell connected to Autolab PGSTAT 30 potentiostat (Eco Chemie BV) was used to perform the electrochemical measurements aiming at either determining the sulfur solubility or growing sulfides thin films. Depending upon the targeted Co or Fe-based sulfides, the electrolytic bath consists of different molar ratios of Co(TFSI)$_2$ (99.5%, Solvionic) or anhydrous FeCl$_3$ (Fisher Scientific) respectively, together with sulfur powder (99.5%, Alfa Aesar) in the ionic liquid [EMIm]TFSI (99.5%, Solvionic). The working electrode is either a platinum wire (d = 0.5 mm, Goodfellow) or a rotating disk electrode (d = 3 mm) for CV measurements, or a platinum disk (1.25 cm^2) for synthesis. A platinum

foil (400 mm^2) and a silver wire were used as counter and quasi-reference electrodes, respectively. Otherwise specified, all the potentials reported in this thesis are all versus Ag quasi-reference. For the sulfur vapor measurement, the sulfur containing [EMIm]TFSI baths were put in a 35 ml vessels and heated by microwave (CEM μwaves), and then their vapor were monitored and recorded by Discover SP system with ActiVent Pressure Device. For the easy presentation in this paper, the value of the amount of sulfur in the bath will be presented in an equivalent concentration (n_{sulfur}/V_{bath}), e.g. 0.05 M S$_8$ would be presented if 0.25 mmol sulfur is added in 5 ml ionic liquid.

The X-ray diffraction patterns of the samples were collected on a Bruker D8 diffractometer using a Co Kα radiation at 25 °C. The morphology and chemical composition of the samples were studied by field-emission gun scanning electron microscopy (FEI Quanta 200F) fitted with Energy Dispersive X-ray Spectroscopy (EDS). The mass of films is determined by the weight difference of the Pt substrate before and after deposition within the accuracy of 0.01 mg. All electrochemical tests were conducted by VMP controller system (Biologic SA) in a coin-cell configuration with the electrodeposited sulfide films as the positive electrode at 25 °C. The cells were assembled in an argon-filled glove box, using lithium foil as the negative electrode separated by a glass fiber sheet soaked in 1 M LiTFSI in tetra methylene sulfone.

3. Results and discussion

3.1. Solubility of sulfur in [EMIm]TFSI

Soluble precursors are essential for successful electrochemical synthesis, hence the importance to check the solubility of available precursors before performing synthesis. Along that line, knowing the maximum quantity of sulfur that can be dissolved in ionic liquids is essential to properly adjust metallic salts/sulfur ratio in the electrolytic bath and thus better control the electrodeposition process of sulfides.

We first attempted to determine the sulfur solubility in ionic liquids by cyclic voltammetric (CV) measurements. For such purpose 0.25 mmol sulfur were placed in a closed cell containing 5 ml ionic liquid [EMIm]TFSI under stirring above the melting point (120 °C), as the scheme shown in Fig. 1a. Therefore, we must note that the equilibria between all forms of molecular sulfur (including dissolved in the solution, liquid, vapor and remaining solid sulfur) and ionic liquids are complicated processes (Fig. 1b). Most of the solid sulfur is melted and within the ionic liquid solution, there is equilibrium between the liquid sulfur drops and the soluble sulfur species that we denoted as [S$_x$] detected by CV measurements.

Fig. 2a displays CV curves scanning at different rates within the potential range between −1 V and 0.2 V, when 12.5 mM sulfur was added to the solution at 120 °C. Pronounced reduction/oxidation peaks of sulfur were observed, revealing the solubility of molecular sulfur in [EMIm]TFSI at this temperature. The increase in ΔE_p (between cathodic peak potential E_{pc} and anodic peak potential E_{pa}) with the increase in scan rate (v) is observed, which is characteristic of an irreversible process [49]. For an irreversible process, it is known that E_p is linear with lgv with a slope of 1.15RT/αnF (V), where α is the transfer coefficient and n is the number of exchange electrons. So the plot of E_p versus lgv gives the transfer coefficient value of 0.556, although it is close to the reversible value of 0.5. By assuming the irreversibility of the reduction process, equation (1) could be applied to describe the relationship between peak current I_p and the scanning rate v [49].

$$I_p = (2.99 \times 10^5)\alpha^{1/2}n^{3/2}AD^{1/2}v^{1/2}C \tag{1}$$