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Characteristics of glyme electrolytes for sodium battery: nuclear magnetic resonance and electrochemical study

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A B S T R A C T

Glyme electrolytes are prepared by dissolving sodium trifluoromethane sulfonate ($NaCF_3SO_3$) either in dimetoxyethane (DME) or in diethyleneglycoledimethylether (DEGDME). The solutions, designed for sodium battery applications, are thermally characterized by TGA and studied in terms of transport properties by combining pulse field gradient nuclear magnetic resonance (PFG NMR) and electrochemical techniques. Both electrolytes reveal suitable characteristics for sodium batteries, such as ion conductivity of about $10^{-3}\,S\,cm^{-1}$, sodium transport number of 0.5, a stable stripping-deposition trend, and electrochemical stability windows extending from 0 to 4 V. However, the more volatile DME leads to a higher ion association degree. The suitability of both electrolytes is then verified in sodium-sulfur cells by cyclic voltammetry and galvanostatic test. The measurements confirm the reversibility of the sodium-sulfur process, and reveal the expected trend of the sulfur electrode in sodium cell with average working voltage of about 1.8 V, with a higher polarization and lower capacity for the cell using the DME-based electrolyte. Accordingly, the DEGDME-based solution appears to be more suitable for sodium battery applications.

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1. Introduction

Sodium, because of its ubiquity as the 6th most abundant element in the earth's crust, is readily available at low cost. Therefore, batteries based on this alkali metal appear among the most promising systems in view of a widespread application of grid energy storage from renewable sources, such as solar and wind [1–4]. Sodium batteries using intercalation materials have been studied alongside lithium batteries during the late 1970s and 1980s [5–7]. However, the higher energy content of lithium as compared to sodium promoted the rapid development of the lithium-ion systems to the detriment of sodium-ion technologies. Nowadays lithium-ion is the most common type of rechargeable batteries used in the electronic portable devices market and the most promising storage tool for triggering the growth of renewable

energy plants [8,9]. The fast development of the lithium-ion battery actually contributed to a rapid rise of the lithium price [10], and evidenced possible risk of market dependence in view of the geographical limitation of lithium resources to a few South American countries [11]. These issues renewed the interest in non-lithium energy storage systems and, in particular, on sodium batteries, which are presently attracting a large amount of attention. The energy penalty of sodium with respect to lithium [12] may be partially mitigated by the use of high energy cathodes, such as sulfur [6,13,14] which delivers a theoretical capacity of $1700\,mAh\,g^{-1}$ and an energy density of $2500\,Wh\,kg^{-1}$. This high value may translate into a practical energy exceeding $300\,Wh\,kg^{-1}$, higher than that associated with the common lithium-ion battery, as suggested by recent literature focusing on sodium and sodium ion batteries [15–19]. Sulfur–based cathodes have been studied principally for use in lithium batteries [20] following an approach aimed to address issues such as the solubility of the polysulfide discharge products in the electrolytes, and slow kinetics. The studies have achieved relevant progress by the improving the electrode morphology, e.g., by the development of sulfur-carbon

composites with metal layer protection [21], sulfur shielded into mesoporous [22,23] and spherical [24–26] carbon matrix, or by designing polysulfide reservoirs in carbon–sulfur composites [27]. Some of these advanced electrodes, such as that composed by carbon hollow-spheres infiltrated by sulfur, have been successfully employed in a Na/S cell using a glyme-based electrolyte [28]. Glyme-based electrolytes have been recently proposed as suitable electrolyte media for lithium batteries [29], following characterization including various analytical techniques such as NMR, XPS, EIS and other electrochemical methods [30]. Furthermore, solutions of sodium salts in glymes have revealed suitable characteristics allowing their application in sodium and sodium-ion batteries [31–33]. Therefore, we use herein these aforementioned analytical approaches for the study of two solutions of sodium salt (i.e., NaCF$_3$SO$_3$), differing by the glyme used. The solutions, based either on DME or DEGDME, and characterized by NMR and electrochemical techniques, are proposed as suitable media for application in a new sodium sulfur cell. The highest performing cell prototype, using a cathode formed by MWCNTs-sulfur [34] and the solution based on DEGDME, shows a capacity of about 500 mAh g^{-1}, delivered at average working voltage of 1.7 V, hence a theoretical energy density of 850 Wh kg^{-1} and an expected practical energy of interest.

2. Experimental

2.1. Electrolyte

Glyme-based solvents, i.e., 1,2-Dimethoxyethane (CH$_3$OCH$_2$-CH$_2$OCH$_3$) and diethylene glycol dimethyl ether (CH$_3$OCH$_2$CH$_2$)$_2$O, hence DME and DEG, respectively, were purchased from Sigma Aldrich and dried under molecular sieves (Sigma Aldrich, pores diameter 3 Å) for several days until the water content was lower than 10 ppm. The water content was determined by 889 Karl Fisher Coulometer METROHM. Sodium trifluoromethanesulfonate (sodium triflate, NaCF$_3$SO$_3$) and sodium nitrate (NaNO$_3$), by Aldrich, were dried under vacuum overnight at 80 °C. The electrolytes were prepared by dissolving NaCF$_3$SO$_3$ either in DEME and in DEGDME, in a ratio of 1 mol of salt in 1 kg of solvent. The densities of DEME-NaCF$_3$SO$_3$ and DEGDME-NaCF$_3$SO$_3$ were 0.984 and 1.068 g/ml, respectively. The (1m) molality was selected in order to better compare with previous papers and with literature data, while the glyme/sodium ratios are 1:11 and 1:7.5 for DME and DEGDME, respectively. The same solutions were supplemented with a film forming agent (NaNO$_3$, 0.4 mol of salt in 1 kg of solvent) for the final test in a sodium cell. The four solutions, i.e., the bare electrolytes (DME-NaCF$_3$SO$_3$ and DEGDME-NaCF$_3$SO$_3$), and the ones with sodium nitrate (DME-NaCF$_3$SO$_3$-NaNO$_3$ and DEGDME-NaCF$_3$SO$_3$-NaNO$_3$), were prepared and stored in an argon filled glove box with water and oxygen contents lower than 1 ppm.

Thermal gravimetric analysis (TGA) was performed on bare electrolytes by heating the samples under nitrogen flow from 20 °C to 700 °C at 10 °C min^{-1}, using a Mettler Toledo TGA/SDTA85. The self-diffusion coefficients of ^{1}H and ^{19}F nuclei (D$_H$ and D$_F$ respectively), related to the hydrogen in the glyme chain and the fluorine in the CF$_3$SO$_3^-$ anion, were measured with a Bruker 400 Avance III NMR spectrometer using a PFG double-stimulated echo sequence to suppress convection effects in the temperature range from 20 °C to 60 °C. The data were collected every 10 °C with gradient pulses of 1–2 ms, a gradient strength g in the range of 1–45 G cm^{-1}, and a diffusion delay Δ of 100–200 ms. The self-diffusion coefficients of ^{23}Na nucleus (D$_{Na}$) were measured with a Varian 300 WB Direct Drive spectrometer equipped with a DOTY z-gradient probe, using the same double-stimulated echo sequence with gradient pulses of 0.75–1 ms, gradient strength g varied from

2 up to 1000 G cm^{-1} as needed, and a diffusion delay Δ of 12–17 ms. The sodium ion transport number was calculated by using the equation:

$$t^+ = \frac{D_{Na}}{D_{Na} + D_F} \tag{1}$$

where D_{Na} is the self-diffusion coefficient of the Na$^+$ cation and D_F is the self-diffusion coefficient of the CF$_3$SO$_3^-$ anion, as determined by NMR. The electrolyte conductivity was measured by impedance spectroscopy (δ_{EIS}) in a symmetrical stainless steel/stainless steel, 2032 coin-cell equipped by a Teflon O-ring separator, in a 0.1 Hz–0.5 MHz frequency range with signal amplitude of 10 mV using a VERSTAT AMETEC instrument. The impedance responses were collected from 40 °C to 80 °C every 10 °C.

Ion conduction ratio was calculated from self-diffusion coefficient (δ_{NMR}) by using the Nernst-Einstein equation:

$$\delta_{NMR} = \frac{F^2[C]}{RT}(D_{Na} + D_F) \tag{2}$$

where F is the Faraday constant (96485 Coulomb), [C] represents the solution concentration (mol cm^{-3}), and R is the ideal-gas constant (8.314472 J K^{-1} mol^{-1}). The ion association degree (α) was calculated by combining the conductivity values determined by EIS (δ_{EIS}) and the ion conduction ratio determined by NMR (δ_{NMR}), following the equation:

$$\alpha = \left(1 - \frac{\delta_{EIS}}{\delta_{NMR}}\right). \tag{3}$$

The cathodic electrochemical stability of the electrolytes was determined by cyclic voltammetry (CV) in a three-electrode configuration cell using sodium metal as the reference and counter electrodes, and Super P carbon (Imers) coated on copper as working electrode. The CV was performed using a potential ranging from 2 V to 0 V vs. Na/Na$^+$ with a scan rate of 0.1 mV sec^{-1}. The anodic electrochemical stability was determined by linear sweep voltammetry from 2 V to 5 V vs. Na/Na$^+$, using the same cell configuration and scan rate employed for CV, and a Super P carbon (Imers) coated on aluminum as the working electrode. Sodium stripping/deposition tests were carried out in a symmetrical sodium/sodium 2032 coin-cell, with a constant current of 0.1 mA cm^{-2} and a step time limit of 1 hour. The chemical stability of the sodium interface in contact with the electrolyte versus time was studied by impedance spectroscopy (EIS) in a symmetrical sodium/sodium 2032 coin-cell, in a 0.1 Hz–0.5 MHz frequency range, using a 10 mV signal amplitude.

2.2. Sodium-Sulfur cell

The cathode, already proposed for lithium-sulfur cells in a previous paper [34], was formed by mixing elemental sulfur (S, Sigma Aldrich) and multi-walled carbon nanotubes (MWCNs, Sigma Aldrich), in a 1:1 weight ratio, heating at 135 °C in order to melt the sulfur and stirring for 2 hours until complete homogenization. The resulting mixture was cooled at room temperature and treated by high energy ball milling in a stainless-steel jar, with 4 stainless steel balls. The treatment was performed at a frequency of 15 Hz for 2 hours, using 4 steps of 30 minutes of milling and rest steps of 15 minutes. The electrode film was prepared by dispersing the sulfur-carbon powder (S-MWCNs), polyvinylidinedifluoride (PVdF Solvey) binder and Super P (Imers) electron conductor (80:10:10 weight ratio) in N-methylpyrrolidone (NMP, Aldrich), stirring until formation of a homogeneous slurry, casting on aluminum foil by Doctor blade and drying at 50 °C overnight to remove the solvent. Electrode disks were then punched, dried at 50 °C for 24 h under vacuum overnight and introduced in the argon filled glove box to build the cells. The electrochemical reaction of S-