



Dry Solvents for Batteries: Equilibrium Study of Water Adsorption from Dimethyl Sulfoxide using 3A Zeolite

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Research for new and inexpensive energy storage technologies has been increasing in recent years due to the need to store power from intermittent sources such as wind and solar power. Among these advanced energy storage technologies, the Li-O₂ battery is described as a suitable candidate because of its high theoretical energy density. Research has been focused on the development of suitable electrodes and electrolytes to allow high energy density and high cyclability, being the latter one of the main challenges. Poor cyclability is often related to undesirable reactions, and one of the sources of this problem is the presence of water in the electrolyte. Nevertheless, it has been shown that trace amounts of water can also catalyze desirable reaction steps in the operation of a Li-O₂ battery. Therefore, careful control of water content in the electrolyte of Li-O₂ batteries becomes an important task. In this context, this work presents the equilibrium study of water adsorption from dimethyl sulfoxide, a solvent commonly considered for electrolytes of Li-O₂ batteries, using 3A zeolites as the adsorbate. Batch adsorption experiments with different concentrations of water and mass of adsorbate were combined to determine the water removal capacity at different conditions of temperature (20 °C, 35 °C, and 50 °C). Adsorption data were fitted to adsorption models (Langmuir, Freundlich, and Dubinin-Radushkevich) to obtain their constants. Additionally, the regeneration of zeolites was evaluated. These data have the potential to be used by other researchers in the development of Li-O₂ batteries with electrolytes with precisely controlled water content.

1. Introduction

The increased use of renewable intermittent energy sources such as solar and wind power and the increasing deployment of electricity in transport has increased the demand for affordable energy storage options. In this context, batteries represent a reliable option because of their current development state. Currently, the cost of many battery options still hampers specific low-cost applications, such as bulk energy storage for the grid (Schmidt et al., 2019). Therefore, other battery chemistries with the potential to decrease installation costs have been being investigated, such as metal-air batteries (Tan et al., 2017). Among these, Li-O₂ batteries represent a promising candidate because of their potential high energy density. At this time, many efforts are being dedicated to finding suitable combinations of electrode material and electrolyte composition to render a stable device with great energy density and long-lasting cyclability (Imanishi and Yamamoto, 2019).

The electrolyte of a battery must be stable in a wide range of potential and must provide a means of transporting electrochemically active species inside the porous electrode (Gittleson et al., 2017). This electrolyte is majorly composed of a solvent, in which the supporting electrolyte salt is dissolved. Among the many candidate solvents to be used in aprotic electrolytes for Li-O₂ batteries, dimethyl sulfoxide (DMSO) is a suitable option because of the high O₂ and Li⁺ diffusivity and because of its large potential window (Laoire et al., 2010). Besides these characteristics, in the case of Li-O₂ batteries, the water content of the electrolyte solution must be carefully controlled (Wu et al., 2015). This is necessary because, even though there are reports that water can act as a redox mediator, the reaction of water with lithium decreases battery lifetime (Aetukuri et al., 2015; Li et al., 2015).

DMSO is a highly hygroscopic solvent. Even though water can be easily separated from DMSO via distillation because of the very different normal boiling points, the desired water content (10-1000 ppm) needs to be achieved by means of other separation methods. Among possible methods, molecular sieves have been being used on a laboratory scale because of their high efficiency and recyclability (Lepoivre et al., 2016; Shui et al., 2013), but at conditions that are far from ideal to minimize their use and without a methodology to precisely control the water content. Therefore, this work analyzes the use of zeolite 3A for the drying of DMSO to be used in the preparation of electrolyte solutions. Besides an analysis of equilibrium conditions to determine adequate proportions of zeolite to solvent to achieve a desirable water content at equilibrium conditions, this study includes an analysis of the regeneration process for the zeolite under different conditions.

2. Methodology

2.1 Batch adsorption experiments

Adsorption trials were performed in three temperatures (20 °C, 35 °C, and 50 °C) for 24 h without agitation. In each trial, 20 g of DMSO (Nuclear, purity 99.9%) were added to 0.5, 1.0, 2.0, 5.0, 10, and 20 g of 3A zeolite (Sigma-Aldrich, beads, 8-12 mesh). The trials were conducted in sealed flasks immersed in a thermostatic bath (MA 108/9, Marconi Ltda, Brazil). The water content of liquid samples before and after adsorption trials was analyzed in triplicate via Karl Fischer titration (852 Titrando Metrohm AG, Switzerland) in a cell with a diaphragm because of the potentially low concentration of water. The anolyte solution was Hydralan Coulomat AG (Honeywell Fluka) and the catholyte solution was Hydralan Coulomat CG (Honeywell Fluka). The amount of water adsorbed by the zeolite was calculated via mass balance.

2.2 Adsorption models

Adsorption data were fitted using OriginLab 2019b (2019, OriginLab Corporation) to the following adsorption models: Langmuir Eq. (1), Freundlich Eq. (2), and Dubinin-Radushkevich Eq. (3) (Lima et al., 2014).

$$q_e = \frac{q_{max} K_L C}{1 + K_L C} \quad (1)$$

$$q_e = K_F C^{1/n} \quad (2)$$

$$q_e = q_{max} \exp(-K_{DR} \varepsilon^2) \quad (3)$$

in which q_e is the ratio between the mass of water adsorbed and the mass of adsorbate (obtained from the mass balance of initial and final concentration of water in samples and the volume of the sample), q_{max} is the maximum monolayer adsorption capacity, K_L is the Langmuir isotherm constant, C is the equilibrium concentration, K_F is the Freundlich isotherm constant, $1/n$ is the adsorption intensity, K_{DR} is the Dubinin–Radushkevich isotherm constant, and ε is the Polanyi potential, given by Eq. (4). The mean adsorption energy for water can be calculated using the Dubinin–Radushkevich isotherm constant through Eq. (5). For this reason, values of concentration used in all the previous equations must be given in units of mol L⁻¹ (Zhou, 2020).

$$\varepsilon = RT \ln(1 + 1/C) \quad (4)$$

$$E = 1/\sqrt{2K_{DR}} \quad (5)$$

in which R is the universal gas constant (8.314 J mol⁻¹ K⁻¹) and T is the temperature. Enthalpy (ΔH), entropy (ΔS), and Gibbs free energy (ΔG) of adsorption were calculated using Eq. (6), in which K_d is the distribution coefficient (dimensionless) between adsorbate and solution phases at a constant adsorption capacity q_e .

$$\ln(K_d) = -\frac{\Delta G}{RT} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (6)$$

2.3 Regeneration of zeolite

After use in the adsorption trials, the zeolites of all trials were mixed and separated into four batches to follow different treatment procedures before regeneration: a) the zeolite was regenerated without any additional treatment; b) the zeolite was thoroughly washed with type I water (resistivity > 18.2 MΩ·cm) to remove DMSO; c) the zeolite was washed with ethanol (Dinâmica, purity >99.5%) in a proportion of 1:1 in apparent volume to

remove DMSO; and d) the zeolite was washed with ethanol in a proportion of 1:1 in apparent volume and then thoroughly washed with type I water to remove DMSO and ethanol. To simulate the effect of heating to remove the adsorbed water during regeneration of the zeolite, 2 g of zeolites from each washing procedure were ground in a mortar, homogenized, and analyzed via thermogravimetric analysis, differential thermal analysis, and differential scanning calorimetry (TGA, DTA, and DSC, TGA/DSC1, Mettler-Toledo GmbH, Switzerland) up to 500 °C at a heating rate of 10 °C min⁻¹ and under synthetic air (Gabruš et al., 2015). The sample size of each run was ~10 mg (MX5, Mettler-Toledo GmbH, Switzerland). The zeolite before use was analyzed as well (named as sample e).

3. Results and Discussion

3.1 Adsorption of water from solvent

Results of adsorption of water from DMSO are available in Figure 1. According to the results, lower temperatures increase the uptake of water by the zeolite, a behavior which is also observed in systems using 3A zeolites with other solvents (Carmo and Gubulin, 1997). For a solvent with a starting concentration of 1126 ± 9 ppm of water, a zeolite loading of 1 g in 20 g of solvent is enough to decrease the water content of the solvent to 445 ± 5 ppm (at 20 °C). Results of adsorption trials using 10 g and 20 g of zeolite to each 20 g of solvent were inconsistent because they presented water content higher than the trials with 5 g of zeolite — and the discrepancy increased with temperature. In this case, a kinetic study of the adsorption process at high zeolite loading is necessary to evaluate the stability of the solvent. Based on these observations, the drying process should be carried out with small proportions of zeolite to solvent and in subsequent steps, in which the wet zeolite is removed from the solution after equilibrium is reached.

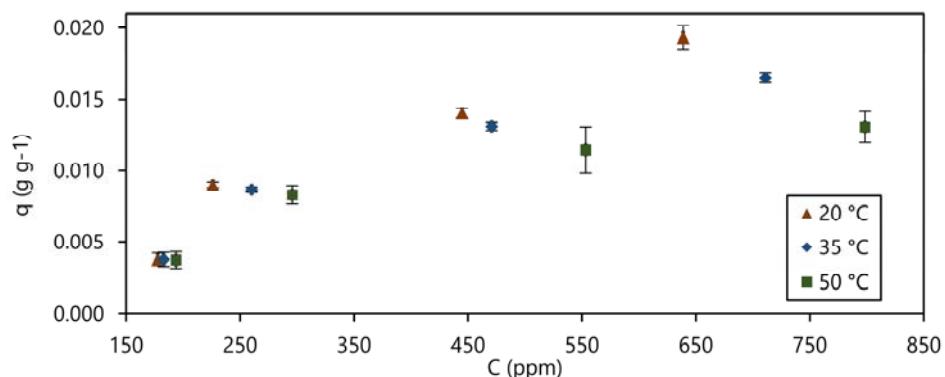


Figure 1: Results of adsorption trials at different temperatures

3.2 Assessment of adsorption models

Table 1 presents the results of data regression for the Langmuir, Freundlich, and Dubinin-Radushkevich models. Based on the analysis of the correlation coefficient, the data fits best the Dubinin-Radushkevich model. According to this model, the mean adsorption energy for water is less than 8 kJ mol⁻¹, thus indicating that physisorption is the predominant sorption mechanism (Argun et al., 2007). The maximum adsorption capacity observed in the Langmuir and Dubinin-Radushkevich is below the range of the maximum adsorption capacity reported for 3A zeolite in other systems probably because of the low water concentration range in which the analysis was carried out (100-1000 ppm). Other studies consider water concentrations up to 100% to completely saturate the zeolite adsorption capacity (Carmo & Gubulin, 1997; Gabruš et al., 2015), but in this case, there is a high influence of the low water concentration in DMSO and the hygroscopic nature of DMSO. Based on the experimental data, the distribution coefficient for a constant q_e of 0.01 g g⁻¹ was estimated for each temperature. The plot of $\ln(K_d)$ versus $1/T$ yields a straight line with a correlation coefficient of 0.95. Based on this data regression, the enthalpy of the adsorption process was calculated: -8.9 kJ mol⁻¹. The negative enthalpy indicates that the process is exothermic. In fact, adding a single drop of water to a small amount of zeolite releases a considerable amount of heat. This observation is confirmed by the desorption peak observed in Figure 4, which indicates that water desorption from the zeolite is an endothermic process.

Table 1: Results of data regression for Langmuir, Freundlich, and Dubinin-Radushkevich models.

T (°C)	Langmuir			Freundlich			Dubinin-Radushkevich			
	q _{max} (g g ⁻¹)	K _L (L mol ⁻¹)	R ²	K _F	n	R ²	q _{max} (g g ⁻¹)	K _{DR} (mol ² J ²)	E (J mol ⁻¹)	R ²
20	0.2166	2.5304	0.949	0.439	1.04	0.947	0.0775	2.09×10 ⁻⁸	4891	0.954
35	0.0576	9.5694	0.946	0.228	1.21	0.935	0.0538	1.74×10 ⁻⁸	5363	0.953
50	0.0276	0.0012	0.927	0.104	1.49	0.900	0.0332	1.31×10 ⁻⁸	6167	0.925

Based on the regressed parameters, it is possible to estimate the water content of solvents after drying in a multistep process. For instance, for a solvent with a starting water concentration of 1500 ppm, the first drying step with 10 g of solvent and 1 g of zeolite would reduce the water concentration of the solvent to 320 ppm. The other two steps (with the removal of the wet zeolite from the previous step and the addition of 1 g of dry zeolite) would decrease the water content to 79 ppm in the second step and 27 ppm in the third step. The heat released in this process is small because of the low water concentration: in the first step of the drying process, the heat released during the water adsorption would raise the temperature of the solvent by 0.3 °C.

3.3 Reuse of zeolite

Figures 2, 3, and 4 show the results of TGA, DTA, and DSC, respectively, of the five samples of zeolites (named a–e, section 2.2). The zeolite before use shows the lowest weight loss upon heating (Figure 2, sample “e”, loss of 7.4 wt% at 500 °C). This weight loss corresponds to humidity that was adsorbed from the environment probably during comminution before analysis. The initial weight gain is minimal and, according to Figure 4, the heat flow during this stage of the heating process is constant — thus, no phase change or phase transition is occurring. Analysis under a different atmosphere might clarify the source of this weight gain. The peak in the range 100–200 °C (Figures 3 and 4) is the only peak observed in all samples, including sample “e” which was not contacted with DMSO. Therefore, this endothermic peak can be attributed to the desorption of water. According to the literature, this temperature range corresponds to water bound to oxygen inside the α -cages of the zeolite (Vučelić et al., 1976). Samples “b” and “d” correspond to situations in which excess water was used in the washing step. Therefore, the peak in the range 25–80 °C corresponds to the vaporization of this excess water which was not adsorbed. Assuming that washing the zeolite with water or ethanol removes all DMSO, the peak observed in the range of 75–125 °C in sample “a” in Figures 3 and 4 can be attributed to the vaporization of DMSO. The peak in the range of 50–100 °C in sample “c” corresponds to the vaporization of ethanol. These two peaks present a substantial difference in relative peak height when comparing to other peaks in Figure 3 and Figure 4. This is explained by the specific latent heat of vaporization of DMSO and ethanol, which are about 1/3 of the specific latent heat of vaporization of water. Therefore, a large variation in weight due to vaporization in Figure 3 corresponds to a small variation in heat flow in Figure 4. In Figure 3, two convoluted peaks are observed for sample “d”, and one of these two peaks (at the same temperature range as the ethanol peak in sample “c”) is attenuated in Figure 4 because of the relative difference in specific latent heat of vaporization.

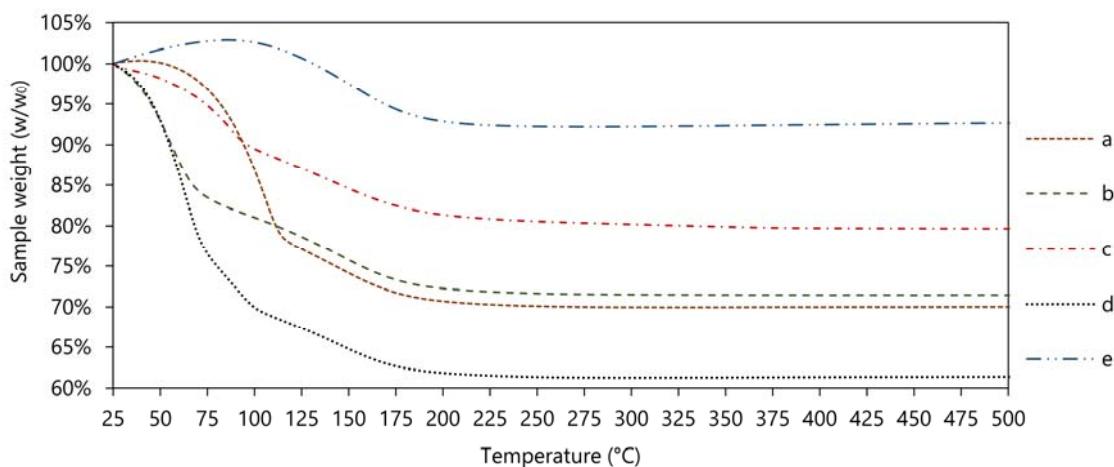


Figure 2: Thermogravimetric analysis curve for the five zeolite samples: a) no washing, b) washed with water, c) washed with ethanol, d) washed with ethanol and water, e) before use

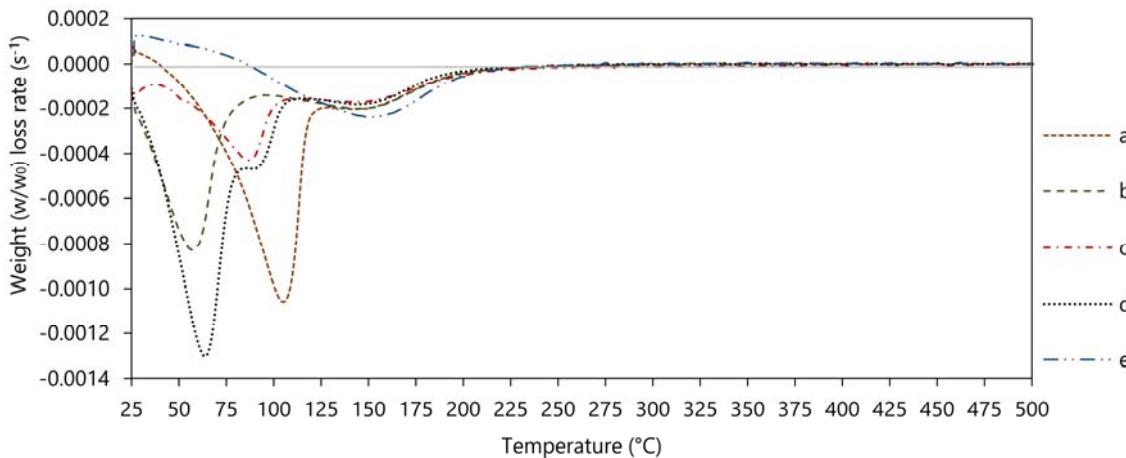


Figure 3: Differential thermal analysis curve for the five zeolite samples: a) no washing, b) washed with water, c) washed with ethanol, d) washed with ethanol and water, e) before use

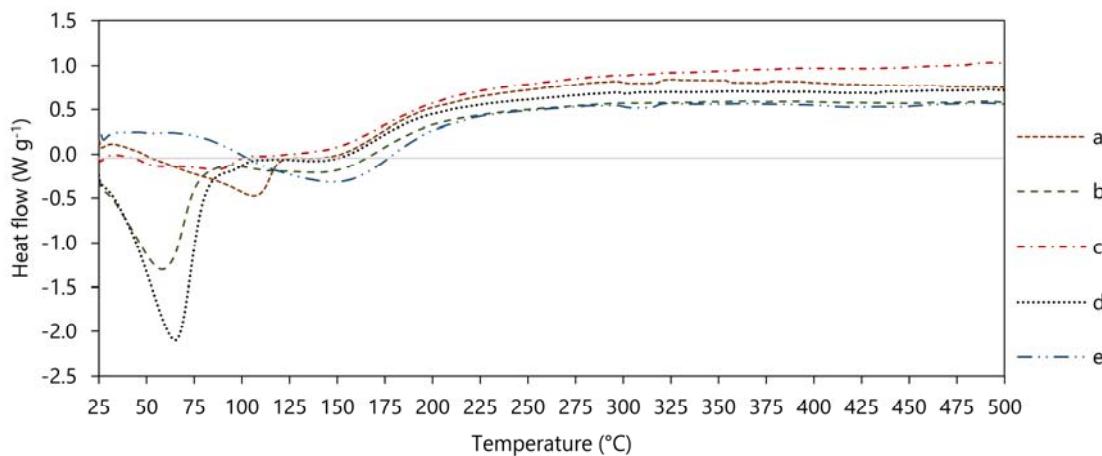


Figure 4: Differential scanning calorimetry curve for the five zeolite samples: a) no washing, b) washed with water, c) washed with ethanol, d) washed with ethanol and water, e) before use

According to Figure 3, most of the matter adsorbed onto the zeolite is removed in temperatures up to 225 °C. The combined use of ethanol and water guarantees that most residues are removed at lower temperatures (<125 °C). The results in Figure 4 indicate that the heat flow is constant for all samples in the temperature range of 300–500 °C, except for some artifacts observed in the range 300–375 °C of sample “a” that, by their shape, indicate a small interference of the electrical network in the analysis. The variation in heat flow in the range of 225–300 °C is very small and might be a consequence of the chosen heat ramp. According to the literature, heating the zeolites above 270 °C might lead to loss of adsorbing capacity (Simo et al., 2009). Therefore, to avoid damaging the zeolite, a temperature of 250 °C is suggested for the regeneration process, and the zeolites do not require washing before regeneration.

4. Conclusions

The development of new batteries will require strict control over the water content of electrolytes. This work demonstrated the possibility of controlling very low water contents in dimethyl sulfoxide using 3A zeolite. Among adsorption models, the Dubinin-Radushkevich showed the best fit for the experimental data. Based on regressed data, it was possible to suggest a multistep approach to solvent drying that minimizes the use of zeolites. The process, though exothermic, does not lead to a large temperature increase because of the low water content of the solvent. Moreover, the water uptake capacity of the zeolite is increased at lower temperatures. Regarding the use of zeolites, the thermogravimetric analysis showed that a temperature as

high as 250 °C is enough to remove all water from the zeolite, and a washing step is not required before regeneration. Overall, the results indicate that it is possible to achieve a precisely low water concentration in electrolyte composition using reduced amounts of 3A zeolite.

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