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Short communication

# Water determination in composite PEO-based polymer electrolytes by volumetric Karl Fischer titration method

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## Abstract

The determination of water in composite poly(ethylene oxide) (PEO)-based polymer electrolytes by volumetric Karl Fischer (KF) titration is described. The measurements have been carried out on specimens (up to 10 g) of polymer electrolytes (as single components, their mixture and thin film) in a dry-room (relative humidity, RH, <0.2% at 20 °C). The use of a dry-room allowed to obtain a baseline drift (defined as the titration rate necessary to keep dry the cell) as low as 0.5 μg $H_2O$ $min^{-1}$. Working range is 0.001–0.5 wt.% $H_2O$ and precision, expressed as relative standard deviation of seven replicates, is 5 at 0.5 wt.% level. Comparison of the gathered results with those obtained by oven methods are provided. Uptake water from surrounding environment can be detected at a level as low as 0.001 wt.%.
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*Keywords:* Volumetric Karl Fischer titration; Polymer electrolytes; Water determination

## 1. Introduction

The determination of water in composite PEO-based polymer electrolytes, used in the technologies of lithium battery, is essential because its presence even at micrograms per gram level is deleterious for the functionality and lifetime of the battery itself. Since the single components of the polymer-based electrolytes are highly hygroscopic, the moisture contamination level has to be kept to a minimum during the preparation, handling and package of these materials. However, the mode and nature of water sorption/desorption of polymer electrolytes have not been studied. Therefore, analytical methods for the determination of water content in composite PEO-based polymer electrolytes, both as simple mixture of components or thin film, are needed.

Drying oven methods (conventional or microwave oven), which depend on the temperature and time parameters chosen, are usually used for the water determination in this kind of electrolytes [1]. However, they suffer from different drawbacks like not selectivity for water. In fact other volatile substances present in the sample or formed during the drying process may contribute to the loss of weight, which may be defined as water [2–5]. Moreover, the heat supplied during drying may be deleterious for the sample integrity.

The Karl Fischer (KF) method is a well-established method for the determination of water [6] based on the Karl Fischer reaction [7]. It is a primary method that determines water in the range $1 \times 10^{-4}$ to 100% at ambient temperature. Nowadays this technique is increasing in popularity in the routine laboratory practice owing to the commercially available automated instruments and ready-to-use new KF reagents, which allow to obtain quick, precise and reliable results [8–10]. To the best of author's knowledge, there are not detailed papers in the literature dealing with the determination of water in composite PEO-based polymer electrolytes by KF technique.

The determination of water in hygroscopic substance will be affected by the humidity of the working environment, especially at very low concentration levels. During sample-handling the possibility of reversible water uptake/release from air may lead to erroneous result of the titration. The measurements should be corrected for the baseline drift (defined as the residual or penetrating moisture that the apparatus

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removes per minute [11]). Ideally, moisture in the atmosphere should be at the same level than the water content in the sample. The use of a room with controlled relative humidity (RH) may prevent the sample to lose as well as gain water, thus improving the accuracy of the result.

In the present paper, a method aimed to determine the total content of water in composite PEO-based polymer electrolytes by volumetric Karl Fischer method is described. The specimens are single components of composite polymer electrolytes, their mixture and thin film, which are prepared and stored under low RH (≤0.2% at 20 °C). Water uptake from surrounding environment can be detected at a level as low as 0.001 wt.%.

## 2. Experimental

### 2.1. Instrumentation

Titrations were performed with a TitriLab™900 automatet KF titration system from Radiometer (Copenhagen, Denmark), which consisted of TIM900 Titration manager control unit, ABU900 20 mL high precise Autoburette Station for the accurate delivery of the titrant (resolution down to 0.1 μL) and SAM90-KF Sample Station, a combined electrode holder and built-in magnetic stirrer, for samples vessel location. The sample vessel with holes for the burette tip, the electrodes, the drying tube and the sample inlet allowed the sample to be protected against exposure to atmospheric moisture. A waste pump is available for automatic emptying of the sample vessel. Desiccator traps were fitted to maintain the atmosphere dry. The emptying of the sample vessel and pre-titration of solvent are automated. The solid samples were introduced through the sample inlet hole using a funnel. The titrations were performed as a dead-stop end-point titration using one double platinum electrode (M21Pt12 Double Platinum Electrode with adapter A94P801) immersed in the solution to be titrated. The electrode is polarised by a constant current of 5 μA during the titration and a stop voltages between 5 and 50 mV were chosen. A predetermined time period between 20 and 60 s, during which no additional titrant is added to the titration vessel, was used as a fixed end point. The minimum and maximum burette speed was set at 0.2 and 2 mL/min, respectively. The KF proportional band was set to 100 mV.

The samples were weighted with a microbalance (AND HM-202) with 0.00001 g accuracy. All the experiments were carried out in dry-room with RH < 0.2% at 20 °C (Corridi S.R.L., Italy).

### 2.2. Chemicals and solutions

The one-component pyridine-free KF reagent equivalent to 1 mg of $H_2O$/mL was purchased from Merck. The two-component imidazole-based KF reagent (hydranal titrant 2 equiv. to 2 mg of $H_2O$/mL) and solvent (hydranal solvent) were purchased from Riedel-de-Haen. The KF reagents were stored in brown tightly closed bottles. Dry methanol (Merck) was maintained over 4 nm molecular sieves, previously regenerated at 350 °C for 24 h. The water equivalent (titer) of the KF reagents was determined using hydranal-water standard 10.0 and daily checked. Working standard water solutions in the concentration range 0.001–0.5 wt.% $H_2O$ were prepared fresh daily by appropriate dilution of deionised water (ultra-high-purity water with a specific resistance of 18.2 MΩ cm obtained from a Milli-Q Gradient water purification system, Millipore, France) in dried methanol and stored in screw cap bottles. Sample sizes were in the range 0.5–10 g and measured by back weighing. Samples were analysed seven times each.

### 2.3. Samples

The preparation of mixture and thin film was carried out in the dry-room and details are described elsewhere [12]. The starting materials were: PEO (poly(ethylene)oxide) (molecular weight $4 \times 10^6$, Union Carbide Corp., Danbury, CT, USA) lithium trifluoromethanesulfonate ($LiCF_3SO_3$) (battery grade, 3 M) and $\gamma$-$LiAlO_2$ (Cyprus Foote Mineral Co., PA, USA).

### 2.4. Procedure

The baseline drift was at first measured under certain conditions as follows. Thirty millilitres of solvent were added to the titration vessel and pre-titrated to dryness. Then, the dried solvent was kept in the vessel (without sample) for 1 h under stirring and subsequently titrated with a stop-delay time of 60 s. The baseline drift, in μg $H_2O$/mL, was calculated from the KF reagent volume added to the working medium to keep the cell dry during the chosen time and taking into account the water equivalent of the reagent.

An accurately weighed sample was introduced into the cell containing 30 mL of pre-titrated solvent and kept to vigorously stirring with magnetic stir as follows:

(i) $LiCF_3SO_3$ for 2 min,
(ii) PEO for 10 min,
(iii) $\gamma$-$LiAlO_2$ for 30 min,
(iv) polymer electrolyte as mixture for 30 min and
(v) polymer electrolyte as thin film for 30 min.

Then, the solution was immediately titrated until the end point is reached. The water content (WC) of sample was calculated using the following equation:

$$WC = V_{KF} W_{eq} \frac{100}{W_{sample}} \tag{1}$$

where $V_{KF}$ is the consumption of titrant in mL, $W_{eq}$ the titer of titrant in mg $H_2O$/mL and $W_{sample}$ the weight of sample in mg. The results were checked by interpolation of the calibration graph (five standards).

### 2.5. Gravimetric analysis

A standard gravimetric method was carried out as follows: PEO and $LiCF_3SO_3$ (1 g) were dried in a vacuum oven at temperature between 50 and 105 °C for 2 h and 120 °C for 5 h, respectively; $\gamma$-$LiAlO_2$ ceramic powder (1 g) was dried in an oven at 300 °C for 5 h. A test for constancy of mass is performed by additional drying steps of 30 min until the difference in mass does not exceed 0.5 mg. The water contents, i.e. the 'loss on drying' (LOD), were calculated using the following equation: water loss (wt.%) = $(a - b)/a \times 100$ where $a$ is the initial weight of sample (g) and $b$ the weight of sample (g) after heat-treatments.

## 3. Results and discussion

### 3.1. Determination of water in $LiCF_3SO_3$, poly(ethylene)oxide (PEO) and $\gamma$-$LiAlO_2$ single components

Preliminary studies using one-component pyridine-free KF reagent showed low drift values, which indicated that the intruding water from surrounding the sample cell is very small. The baseline drift caused by intrusion of ambient moisture in the sample vessel was calculated to be as low as 0.5 μg $H_2O$/min. This drift has been periodically checked, and the results indicated that it was stable during measurements. However, titration using one-component pyridine-free KF reagent leads to prolonged delay time. Different delay times between 20 and 60 s have been investigated and it has been verified that a delay time of 60 s is needed to reach the completeness of titrations. Therefore, it has been chosen to use two-component imidazole-based KF hereafter.

The dissolution of the specimens in the proper solvent is essential for obtaining accurate analytical results. $LiCF_3SO_3$ completely dissolved in hydranal solvent in a few minutes. PEO is soluble both in methanol [13] and in hydranal solvent, even though the solution has a high viscosity. Conversely, $\gamma$-$LiAlO_2$ does not dissolve in hydranal solvent. The only water that can be detected is the water extracted by the organic solvent. The water content in $\gamma$-$LiAlO_2$ has been determined after release for a given time in the hydranal solvent and subsequently titrated using KF reagent.

Table 1 shows the result of the water determination in as-received $LiCF_3SO_3$, PEO and $\gamma$-$LiAlO_2$. Different brands of $LiCF_3SO_3$ have been analysed. The results obtained by drying oven method are also reported in Table 1. The samples have been heated according to the standard conditions in a drying oven at a given temperature and time. Although a reference exists for the LOD of PEO [14], the loss on drying cannot be determined by the simple drying oven method, because the heat supplied during drying provokes decomposition of the sample. Nevertheless, the drying temperature has been set between 50 and 120 °C for different drying times. The LOD results at 50 °C have been the most scattered because during desiccation water is partially removed, whereas the LOD results at 105 °C have been better with standard deviations of 0.001% water. The KF data for the water determination in $LiCF_3SO_3$ and $\gamma$-$LiAlO_2$ well agree with those obtained with drying method. It is worth to note that the KF result for PEO is lower than that obtained with the drying method at 105 °C, denoting that at the drying temperature some deterioration of the sample occurs.

Table 1
Results of water determination (wt.%) in as-received single components of composite PEO-based polymer electrolytes by both volumetric KF titration and drying oven methods

| Component | Gravimetric | KF[a] |
|---|---|---|
| $LiCF_3SO_3$ | | |
| Fluka | 0.352 ± 0.001 | 0.34 ± 0.02 |
| Aldrich | 0.235 ± 0.001 | 0.20 ± 0.01 |
| 3M battery grade | –[b] | 0.010 ± 0.001 |
| PEO | | |
| Drying temperature (°C) | | 0.39 ± 0.02 |
| 50 | 0.305 ± 0.010 | |
| 90 | 0.350 ± 0.008 | |
| 105 | 0.401 ± 0.001 | |
| $\gamma$-$LiAlO_2$ | 0.456 ± 0.001 | 0.40 ± 0.02 |

[a] Two-component imidazole-based KF reagent.
[b] Non-detected.

### 3.2. Determination of water in polymer-based electrolytes both as mixture and thin film

Composite PEO-based polymer electrolytes, both as mixture and thin film, have been prepared starting from the single constituents, previously desiccated, in the dry-room and immediately analysed for the water content. The amount of water found in the samples is as low as 0.001 wt.%. In Table 2 are reported the KF results of the analysis of the same samples stored in plastic envelope, sealed under vacuum and kept in the dry-room for 1 month. As it can be seen the water content in the analysed samples is 0.02 wt.%, indicating that water is absorbed on the dried samples during the sample package and at long-time sample storage in the dry-room.

### 3.3. Analytical figures of merit

The calibration curve has been constructed using deionised water in dried methanol as standard solutions

Table 2
Results of the water determination in composite PEO-based polymer electrolytes, both as mixture and thin film, by volumetric KF titration using two-component imidazole-based KF reagent

| Sample[a] | $H_2O$ (wt.%) | R.S.D. (%) |
|---|---|---|
| Mixture | 0.02 ± 0.002[b] | 10 |
| Thin film | 0.02 ± 0.003[b] | 15 |

[a] Stored in plastic envelope, sealed under vacuum and kept in the dry-room for 1 month.
[b] Mean ± standard deviation of seven replicates.

in the range of concentration 0.001–0.5 wt.% water. The curve is linear over the range studied with correlation coefficient better than $r = 0.9999$ ($n = 5$) with the intercept does not significantly differ from zero [15]. The precision, expressed as relative standard deviation, is better than 5% ($n = 7$) at the 0.5 wt.% level. The water content in composite PEO-based polymer electrolytes both as single component, their mixture and as thin film can be detected in the range as low as 0.001 wt.% using up to 10 g of sample size.

## 4. Conclusions

The determination of water in composite poly(ethylene oxide) (PEO)-based polymer electrolytes, as single components, their mixture and thin film, has been successfully carried out by volumetric Karl Fischer (KF) titration. The use of a dry-room (RH < 0.2% at 20 °C) allowed obtaining a baseline drift as low as 0.5 μg $H_2O$/min. The water content in polymer-based electrolytes can be detected at a level as low as 0.001 wt.% using up to 10 g of sample size. The proposed method is quicker and more accurate than the conventional drying methods for the determination of water in composite poly(ethylene oxide) (PEO)-based polymer electrolytes.

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