



# A lithium iron phosphate reference electrode for ionic liquid electrolytes

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## ABSTRACT

We report on the development of a very simple and robust reference electrode suitable for use in room temperature ionic liquids, that can be employed with planar devices. The reference electrode is based on  $\text{LiFePO}_4$  (LFP), a common cathode material in Li-ion batteries, which is air and water stable. The reference electrode can be drop-cast onto a planar electrode device in a single step. We demonstrate that very low  $\text{Li}^+$  ion concentrations (millimolar or below) are sufficient to obtain a stable and reproducible LFP potential, thus making physical separation between the reference and working electrode unnecessary. Most importantly, the LFP potential is also entirely stable in the presence of oxygen and shows only a very small drift ( $< 10$  mV) in the presence of hydrogen gas, while the potential of a platinum pseudo-reference electrode is shifted  $> 800$  mV. This is the first time that such a stable reference electrode system for ionic liquids has been implemented in miniaturized, planar electrode devices.

## 1. Introduction

Room temperature ionic liquids (RTILs) are a very interesting class of solvent offering unique properties. Their non-volatility and intrinsic ionic conductivity makes RTILs ideal electrolytes for both fundamental electrochemical studies and various applications, especially electrochemical sensing [1,2]. A major challenge of RTIL electrolytes is the lack of a simple and reliable reference electrode [3]. Most electrochemical studies in RTILs rely on bare Pt or Ag wires as pseudo-reference electrodes. The main advantage of such a pseudo-reference electrode is its simplicity, but its potential depends upon surface or electrolyte impurities and is therefore not well defined [4]. This leads to potential drifts over time and hampers reproducibility and comparability between different experiments [5–8]. Ferrocene can be added at the end of an experiment for calibration purposes [3,8,9], but its relatively low solubility [9], moderate volatility [10] and non-innocent nature in the presence of analyte species [8] must also be considered. Additionally, this “post-calibration” method may not be suitable for anything other than simple voltammetric experiments – for example, constant-potential methods, such as long-term chronoamperometry, where potential shifts can occur during the experiment.

To solve this problem, several groups have developed stable reference electrodes for RTILs utilizing redox couples like Ag/AgCl [11], Ag/Ag<sup>+</sup> [12–14], Ag/Ag<sub>2</sub>S [15] and ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) [7]. In most of these designs, the reference electrode is placed in a separate compartment which is ionically connected with the sample

solution by a salt bridge (e.g. glass-fiber filter [7] or glass frit [12,13,15]). On the one hand, this physical separation is necessary to prevent influencing the electrochemistry at the working electrode by ion cross-over from the reference electrode (even Ag/AgCl is somewhat soluble in RTILs [16]). On the other hand, it makes these designs more complicated, rendering them unsuitable for planar electrode devices which would otherwise be very promising platforms for medical and environmental lab-on-a-chip systems [17] and electrochemical sensors [18] because of their small size and low cost.

The goal of this study is the development of a reference electrode for RTIL electrolytes with the following properties: (i) a well-defined and reproducible potential, (ii) a simple assembly suitable for miniaturized devices, (iii) chemical stability towards air and moisture and (iv) potential stability in the presence of oxidizing and reducing gases. The reference electrode is based on lithium iron phosphate (LFP) [19], a well-known cathode material used in Li-ion batteries, which can reversibly de/intercalate Li ions:



The delithiation of  $\text{LiFePO}_4$  is a two-phase reaction with a stable potential over a very broad lithium content ( $x$  in  $\text{Li}_x\text{FePO}_4$ ), thus making it an ideal reference electrode material – it has already been used in Li-ion batteries and ion-selective electrodes [20–24] but not yet in voltammetric experiments in RTILs. The idea involves using a single compartment amperometric cell containing the working, counter and the LFP reference electrode without a separation or diffusion barrier

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(e.g. glass frit) in-between. The major advantage of this one-compartment approach is its simplicity – the LFP powder can be applied to the reference electrode substrate in a one-step drop-casting – and can be easily incorporated into a printing process for mass fabrication. There are two possible problems with this one-compartment approach where the working and the reference electrodes share the same electrolyte solution. Firstly, the potential of the LFP reference electrode depends on the Li-ion concentration in the electrolyte (see Eq. (1)). The presence of a lithium salt, added to the electrolyte to define the LFP reference electrode potential, might impact the electrochemistry at the working electrode. Secondly, reactive analyte species (especially gases) can also reach the LFP reference electrode where they might alter the reference potential. In order to address these two issues, we focus on (i) minimizing the Li-ion concentration necessary for a reproducible LFP potential and (ii) investigating the influence of O<sub>2</sub> and H<sub>2</sub> gases on the stability of the LFP potential.

## 2. Experimental

### 2.1. Preparation of LFP reference electrode

LiFePO<sub>4</sub> (Clariant, Germany) was chemically delithiated to Li<sub>0.5</sub>FePO<sub>4</sub> by stirring it in a 0.05 M aqueous K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (Sigma Aldrich, > 99.0% purity) solution for a few hours [21]. Afterwards, an ink was prepared containing 93 wt-% Li<sub>0.5</sub>FePO<sub>4</sub>, 7 wt-% polyvinylidene fluoride as polymer binder (PVDF, Kynar) and *n*-methyl-2-pyrrolidone (NMP, Sigma Aldrich) as solvent (solid content 0.55 g mL<sup>-1</sup>). The ink was homogenized with a magnetic stirrer for 30 min and drop-cast using an Eppendorf pipette onto a microchip containing three thin-film (150 nm thick) platinum electrodes (ED-SE1-Pt, MicruX, Ovedio, Spain, see Fig. 1a). The NMP solvent was evaporated at 50 °C in a fume hood; the LFP ink was stored in a freezer to prevent sedimentation and could be used for several months. For simplicity, the LFP coating covered all three electrodes on the device (see Fig. 1b), while a separate chip was used for the working and counter electrodes (see Section 2.2 for details).

### 2.2. Electrochemical experiments

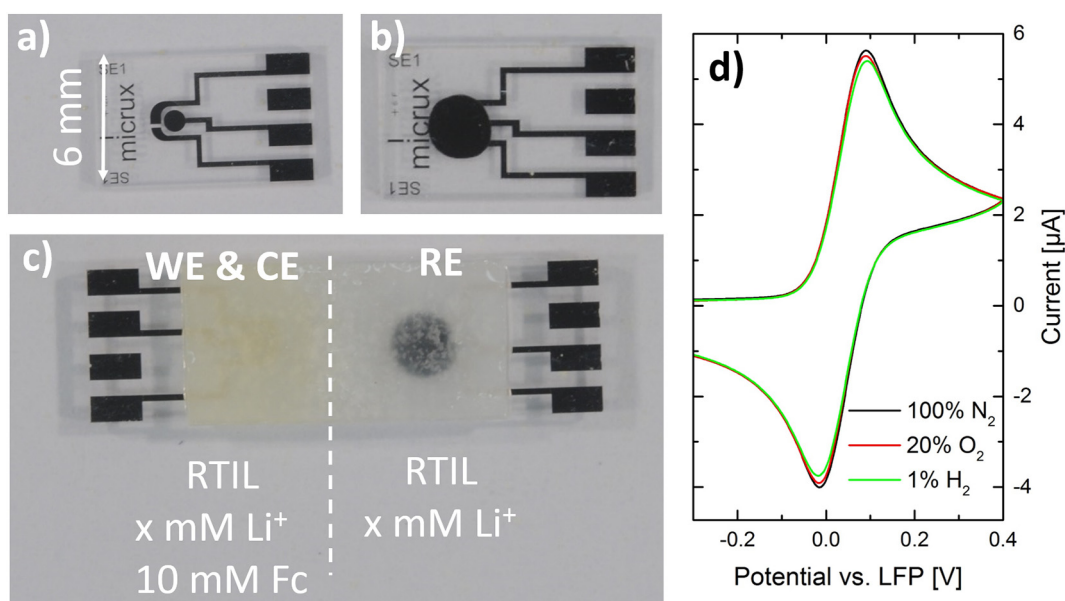
The potential of the reference electrode was determined against the

half-wave potential,  $E_{1/2}$ , of ferrocene/ferrocenium (Fc/Fc<sup>+</sup>), a common redox-couple used as an internal reference in voltammetry [25]. In preliminary experiments, we observed that the presence of ferrocene can alter the open circuit potential of a platinum pseudo-reference electrode. In order to properly assess the potential stability/instability of the platinum pseudo- and the LFP reference electrode, two microchips were used, as shown in Fig. 1c. One chip (left side in Fig. 1c) contained the working and counter electrodes (WE & CE) and the other chip (right side in Fig. 1c) the reference electrode (RE). The electrolyte, kept in place by a glass fiber filter (Whatman, Sigma-Aldrich), consisted of the ionic liquid *N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([C<sub>4</sub>mpyrr][NTf<sub>2</sub>], IoLiTec, 99.0%) and a fixed concentration of lithium bis(trifluoromethylsulfonyl)imide salt (Li[NTf<sub>2</sub>], Sigma-Aldrich, 99.95%). Equal concentrations of Li[NTf<sub>2</sub>] were added to both sides to prevent the formation of a junction potential. The WE & CE chip also contained 10 mM ferrocene (Sigma-Aldrich, 99.0%). After adding the electrolyte, a 6 × 6 mm glass coverslip was placed on top of the glass fiber filter covering the WE & CE chip in order to slow down the diffusion of H<sub>2</sub> to the working electrode. This was necessary as H<sub>2</sub> is oxidized in a similar potential region as ferrocene. The RE chip was not covered, allowing fast gas diffusion towards the reference electrode.

The microchips were contained in a sealed modified glass T-cell [26], which was continuously purged with high purity nitrogen (BOC gas, North Ryde, NSW, Australia, 99.9%) and optionally also 1% vol. H<sub>2</sub> (BOC, 99.9%) or 20% vol. O<sub>2</sub> (BOC, 99.0%). The gases were diluted using the relative ratios of two mass-flow controllers, as described previously [26]. After the assembly, the cell was allowed to equilibrate under N<sub>2</sub> flow for 1 h before measuring cyclic voltammograms every 3 min with a scan rate of 500 mV s<sup>-1</sup> (PGSTAT101, Metrohm Autolab). Fig. 1d shows three selected voltammograms measured either in pure N<sub>2</sub> or in the presence of H<sub>2</sub> or O<sub>2</sub>.

## 3. Results and discussion

Fig. 2a shows the potential of the platinum pseudo- and LFP reference electrodes versus the Fc/Fc<sup>+</sup> potential after 1 h of equilibration. The potential of the platinum pseudo-reference electrode, measured in the same set up shown in Fig. 1c but without the LFP ink, changes by > 50 mV in the initial 60 minute N<sub>2</sub> period. Then, the potential



**Fig. 1.** Microchip with platinum thin-film electrodes (a) as received and (b) with the LFP coating; (c) set up consisting of two microchips, covered by a glass fiber separator containing the electrolyte (the dashed line indicates the boundary between the WE & CE and the RE electrolyte).  $x = 0, 0.1, \text{ or } 1 \text{ mM}$ ; (d) selected cyclic voltammograms ( $500 \text{ mV s}^{-1}$ ) showing the Fc/Fc<sup>+</sup> redox couple in [C<sub>4</sub>mpyrr][NTf<sub>2</sub>] in the presence of different gases.

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