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Original scientific paper

Lignin-based porous junction for silver-silver chloride reference electrodes

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Abstract
Carbonized lignin powder was used as a salt bridge for a silver-silver chloride reference electrode. This easy-to-prepare reference electrode exhibited excellent stability in saturated potassium chloride solution. In addition, the electrochemical impedance spectra showed that the prepared reference electrode is stable in acidic, neutral, and basic aqueous solutions (pH 1 - 12) and has similar impedances to its glass frit equivalent.

Keywords
Porous carbon material, carbonization, impedance spectroscopy

Introduction

A reference electrode with its constant equilibrium potential provides the reference point for each electrochemical measurement. By far the most commonly used reference electrode is the silver-silver chloride electrode, due to its advantageous characteristics like low cost, high stability, reproducibility of potential and electrochemical reversibility [1]. This electrode consists most often of a silver wire coated with silver chloride in a plastic or glass tube with a diaphragm at the end. Here, the diaphragm serves as a salt bridge between the reference solution of the reference electrode and the electrolyte of the system under investigation. Commercially available are junctions made of glass [2-3], polyethylene [4], polytetrafluoroethylene [5-6], aluminium oxide [7], or as agar-based gel electrolyte [8-10]. The most common is the use of glass frits, as they have excellent chemical resistance in many solvents. However, they cannot be used in either strongly alkaline or fluorine-containing solutions. The same applies to diaphragms made of aluminium oxide [11]. Porous Teflon and polyethylene frits can be used here, but the larger pores in these materials can cause the electrolyte solution to become contaminated with the reference solution [12] and their hydrophobicity makes wetting of the frits difficult [13]. Gelled materials, like agar-gel, on the other hand, might suffer from biofouling [13] and cannot be used at temperatures above 40 °C because they decompose thermally [10].

Carbon materials are ideally suited for use in electrochemical systems due to various advantageous properties like high chemical and thermal resistance, good conductivity, controllable porosity etc. [14-17], with bio-based carbons offering additional benefits regarding low cost and sustainability aspects [18-19]. However, it is difficult to produce dimensionally stable carbon materials without the use of large amounts of additives that would affect the electrochemical measurement when using the carbon material as a salt bridge for a reference electrode.

Lignin is the second most abundant biopolymer after cellulose [20] and available in large quantities with an annual production of 70 million tons, however, it is almost completely burnt for energy recovery [21]. Due to the high carbon yield and the fact that it is a renewable raw material, lignin is a promising precursor for the production of carbon materials. It has been used for carbon fibers [22-26], carbon nanofibers [22,27,28] or particulate carbons [29-32]. As lignin partially melts during carbonization [14], these materials usually require a stabilization step or very low heating rates during carbonization in order to avoid structural deformation during thermal treatment [28,33]. However, this also offers the opportunity for preparation of porous structural bodies from lignin. As partial melting does not have to be avoided, in fact it is required for the formation of stable bodies, the conversion to carbons can be done at industrially viable process conditions.

Previous work testing carbon materials as diaphragms for reference electrodes have used commercial carbon materials such as drawing charcoal or pencil lead [11,34], the composition of which is not known. In addition, these materials cannot be optimized to meet the desired requirements, since it is difficult to optimize the carbon structure, especially the formed pore structure, after the carbonization step.

Based on the mentioned drawbacks of frequently used glass frits, the promising results using carbon materials and the possibility to easily prepare bio-based porous carbon bodies, in this work, lignin powder is carbonized and investigated as a salt bridge for a silver-silver chloride reference electrode. The electrochemical performance is tested in different solutions and compared with a commercial glass frit.

Experimental

All solutions were prepared from reagent-grade chemicals and ultrapure water. The softwood kraft lignin Indulin AT (Ingevity, USA) was used without any further purification. A commercial Ag|AgCl|sat. KCl reference electrode (6.0726.110, Metrohm AG, Switzerland) was used for the comparative investigations.

For the preparation of porous junction, 50 mg of the kraft lignin Indulin AT was placed in a hole with a diameter of 6 mm, which was previously drilled into a graphite plate. In this cast, the lignin was carbonized at 850 °C with a heating rate of 1 °C min^{-1} in nitrogen atmosphere. The sample was kept isothermal at the target temperature for 30 min before cooling.

Silver chloride was deposited electrochemically on a silver wire (diameter 1.0 mm, purity 99.9 %) in 1 M HCl. The electrode was first cleaned and roughened by cycling 10 times between 0.5 V (against standard hydrogen electrode (SHE)) and -0.1 V (SHE) with a scan rate of 10 mV s^{-1}. Afterwards, silver chloride was deposited by polarizing to 0.1 V (SHE) for 120 s and finally to 0.3 V (SHE) for 600 s. After rinsing with deionized water and drying in air the wire was ready for use. The coated silver wire was placed in a polyurethane (PU) housing and closed at the top with a lid equipped with a connector (Figure 1). Either the carbonized lignin or a glass frit (4 nm pore size, Gamry Instruments Inc., USA) was attached to the bottom of the PU housing as a porous junction using a heat-shrinkable tube. Saturated KCl solution was used as the electrolyte.

The morphology of the carbonized lignin sample was investigated using the scanning electron microscope Phenom ProX (Thermo Fisher Scientific Inc., USA). The used acceleration voltage was 15 kV and a backscattered electron detector was employed.

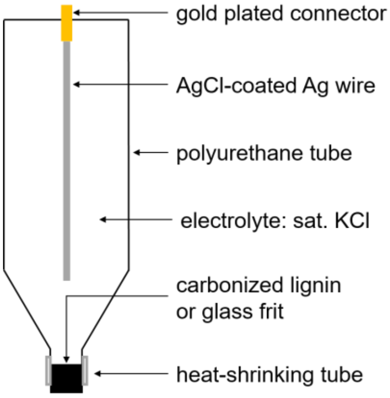

Figure 1. *Schematic representation of the reference electrode used*

Stability measurements on the constructed reference electrode were performed in a 2-electrode setup against the commercial reference electrode transiently in saturated KCl for 200 ks (≈55.6 h). Electrochemical impedance spectroscopy (EIS) was initially performed at the open circuit potential of the electrode in saturated KCl in a 2-electrode setup. For other solutions, a 3-electrode setup was used with graphite as the counter electrode and the commercial Ag|AgCl|sat.-KCl electrode as the reference. An amplitude of 10 mV was always used. The potentiostat Vertex.One (Ivium Technologies BV, The Netherlands) was used for all electrochemical measurements.

Results and discussion

Carbonization of the lignin powder in the cast resulted in a molded body with a diameter of about 5 mm and a height of about 7 mm. The morphology of the sample was examined by SEM (Figure 2).

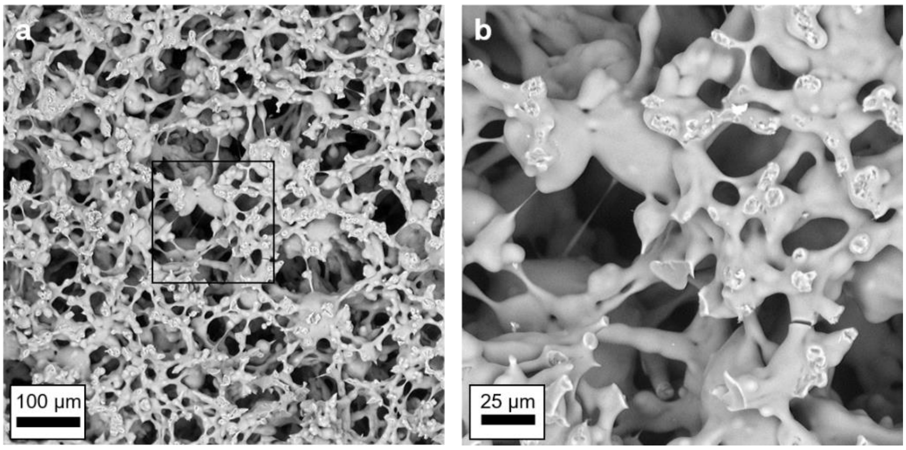

Figure 2. *SEM images of the carbonized lignin; the black box in (a) represents the zoom shown in (b)*

The SEM images show that the carbon body is highly porous. Presumably, the lignin particles melt during carbonization and crosslink, which leads to the structure of the carbon body. The conversion of lignin to carbon occurs with the formation of volatile gases [35], which contribute to the formation of high porosity. In this way, pores are created that range from a few nanometers to several hundred micrometers in diameter.

To characterize the fabricated reference electrode with the carbon diaphragm, its open circuit potential was measured against a commercial Ag|AgCl reference electrode in saturated KCl for 200 ks (≈55.6 h), with the open circuit potential of the cell showing just minor variation in the range of -0.5 – 1 mV. These negligible oscillations in the measurement process can be attributed to the temperature of the laboratory. Otherwise, the potential is very stable over the observed time period.

Electrochemical impedance spectra were first recorded using the reference electrode with the carbonized lignin, then with the glass frit as a salt bridge in a 2-electrode setup against the commercial reference electrode in saturated KCl. The Bode plot (Figure 3) shows both the magnitude of the impedance and the phase angle in the frequency domain. The reference electrode with the carbonized lignin as a salt bridge shows a higher impedance than the electrode with glass frit over the entire observed frequency range. It achieved an impedance of 21.5 – 18.7 kΩ, while an impedance of 20.0 – 17.5 kΩ was reached using glass. The higher impedance of the carbon frit can probably be attributed to its greater thickness. The phase shift is very similar for both electrodes and does not exceed -2°. These only minor differences, show that the carbonized lignin is well suited for use as a diaphragm instead of glass frits in Ag|AgCl reference electrodes.

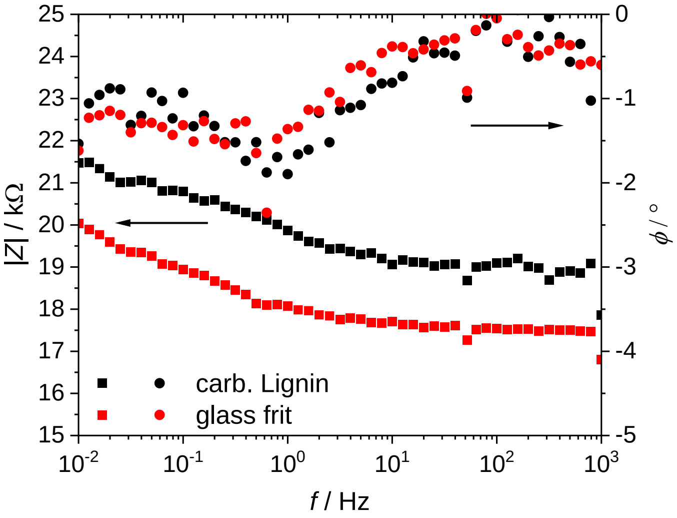

Figure 3. *Bode plot of EIS measurements on the Ag|AgCl reference electrode with carbonized lignin (black) or glass frit (red) as the junction. The measurement was carried out against a commercial Ag|AgCl reference electrode in sat. KCl*

The constructed reference electrode was investigated with both, the carbonized lignin and the glass frit as a salt bridge in different solutions (0.1 M H_2SO_4, 0.1 M citrate buffer, 0.1 M Na_2SO_4, and 0.01 M KOH) against a graphite rod with a commercial Ag|AgCl|sat. KCl reference electrode (Figure 4). In all solutions, a decrease in impedance with increasing frequency is observed, regardless of the junction. Significantly higher impedances are achieved with the carbon membrane than with the glass frit in all the solutions investigated. The phase shift of the diaphragm made of carbonized lignin is slightly higher than that of the glass frit, but does not exceed -7.5°. In the case of the alkaline 0.01 M KOH solution, both junctions show a small phase shift of up to -4°. With longer measurements in the alkaline solution, the glass frit would dissolve [16], which shows a clear advantage for the use of carbon materials as salt bridge for reference electrodes.

Comparing the values of the impedance in Figure 3 and Figure 4, large differences can be spotted. In Figure 3, EIS was measured in a 2-electrode setup in which the impedance of the glass frit or carbonized lignin were measured against a commercial reference electrode. In Figure 4, a 3-electrode setup involving additionally a graphite rod as counter electrode was used. In the 2-electrode setup, in which a commercial reference electrode is both a reference and a counter electrode, the resistance values are higher, because the frit in a reference electrode has larger impedance than the carbon rod counter electrode in the 3-electrode setup. Therefore, larger impedance is measured [36,37].

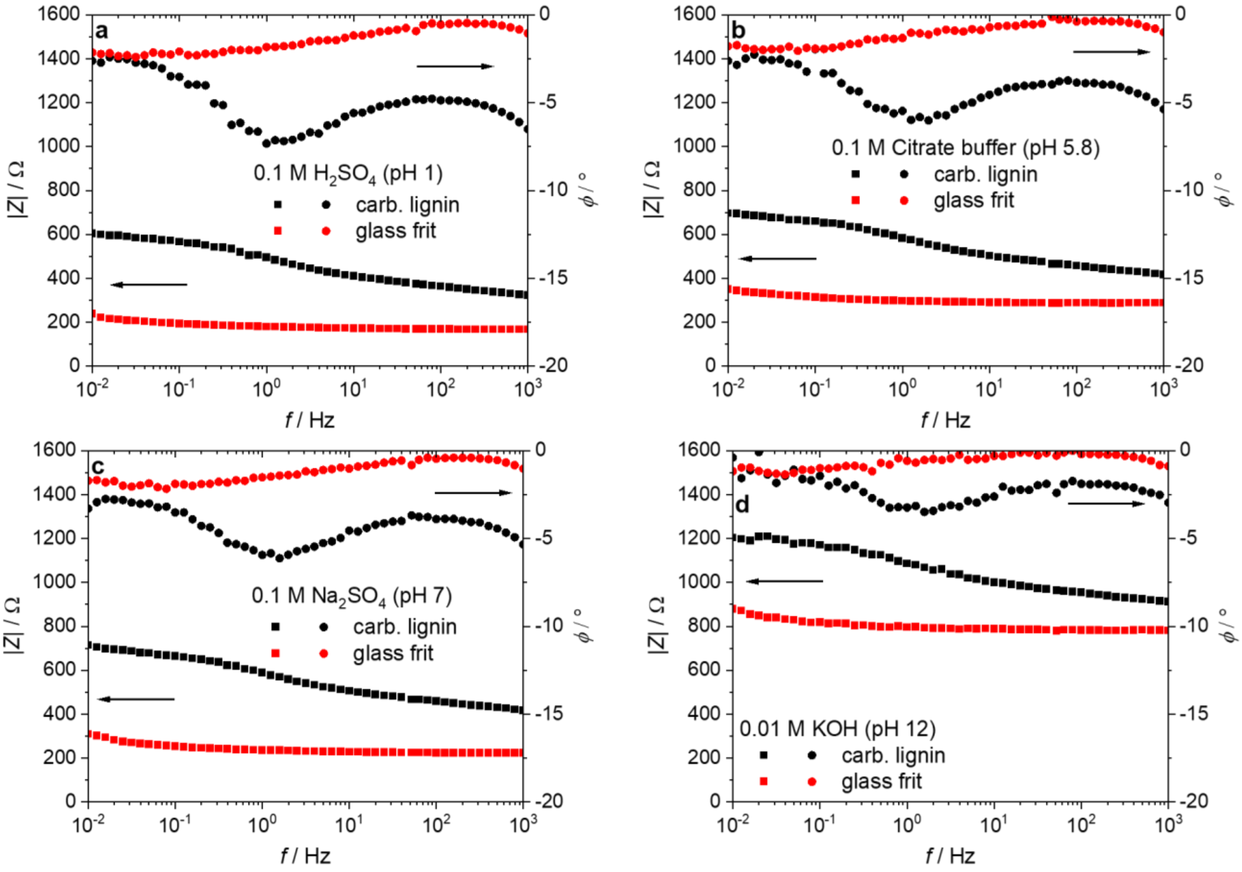

Figure 4. *Bode plot of EIS measurements on the Ag|AgCl reference electrode with carbonized lignin (black) or glass frit (red) as the junction. The measurement was performed against a graphite rod with a commercial Ag|AgCl reference electrode in 0.1 M* H_2SO_4 *(a), 0.1 M citrate buffer (b), 0.1 M* Na_2SO_4 *(c), and 0.01 M KOH (d)*

Conclusions

An Ag|AgCl reference electrode was successfully prepared with carbonized lignin as a salt bridge instead of a glass frit. This reference electrode exhibits excellent stability in saturated KCl. In acidic to weakly basic solutions, it exhibits similar behavior to the equivalent with glass frit. The carbon salt bridge has the advantage that it is very inexpensive to produce and sustainable due to the use of a bio-based waste product as precursor material. In addition, the carbon salt bridge can presumably be used in systems in which a glass frit cannot be used, such as in strong alkaline solutions. The porosity of the carbon can be easily adjusted by the carbonization process and thus tailored and optimized by an additional activation. Based on the reported results, the lignin-based porous carbon junction might be a sustainable, low-cost alternative to currently used glass frits showing already similar performance. However, possible advantages like usability in strong alkaline media need further investigations. Optimization of the carbon with respect to the pore structure and the use of the reference electrode in a larger variety of measurement conditions will be the subject of future studies.

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