Ion-Selective Electrodes Hot Paper

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Intercalation Compounds as Inner Reference Electrodes for Reproducible and Robust Solid-Contact Ion-Selective Electrodes

*Yu Ishige, Stefan Klink, and Wolfgang Schuhmann**

Abstract: *With billions of assays performed every year, ion-selective electrodes (ISEs) provide a simple and fast technique for clinical analysis of blood electrolytes. The development of cheap, miniaturized solid-contact (SC-)ISEs for integrated systems, however, remains a difficult balancing act between size, robustness, and reproducibility, because the defined interface potentials between the ion-selective membrane and the inner reference electrode (iRE) are often compromised. We demonstrate that target cation-sensitive intercalation compounds, such as partially charged lithium iron phosphate (LFP), can be applied as iREs of the quasi-first kind for ISEs. The symmetrical response of the interface potentials towards target cations ultimately results in ISEs with high robustness towards the inner filling (ca. 5 mV dec*$^{-1}$ *conc.) as well as robust and miniaturized SC-ISEs. They have a predictable and stable potential derived from the LiFePO*$_4$*/FePO*$_4$ *redox couple (97.0 ± 1.5 mV after 42 days).*

Ion-selective electrodes (ISEs) are potentiometric sensors for the selective determination of target ions in unknown samples. Their applications include the routine detection of a variety of ions, such as Li^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+, Cl^-, or H^+, in blood, biological, environmental, or process control media.[1] ISEs usually consist of an inner reference electrode (iRE), such as a Ag/AgCl electrode, an ion-selective membrane (ISM) as recognition element, and an inner filling solution (IF) in between. The ISM is typically a liquid polymer membrane containing an ionophore which selectively binds to the target cation I^+ or anion I^-. The inner filling contains at least the target cation or anion and chloride ions in defined concentrations. The half-cell potential $E_{\mathrm{ISE}}^{\mathrm{AgCl}}$ [Eq. (1)] then consists of the potential of the iRE $E_{\mathrm{AgCl,IF}}^{\mathrm{Cl^-}}$ and the potential across the ISM (see Figure 1 a):

$$E_{\mathrm{ISE}}^{\mathrm{AgCl}} = E_{\mathrm{AgCl,IF}}^{\mathrm{Cl^-}} + E_{IF,m}^{I} + E_{m,s}^{I} \qquad (1)$$

where $E_{IF,m}^{I}$ and $E_{m,s}^{I}$ are the interface potentials of the membrane towards the inner filling and sample, respectively.

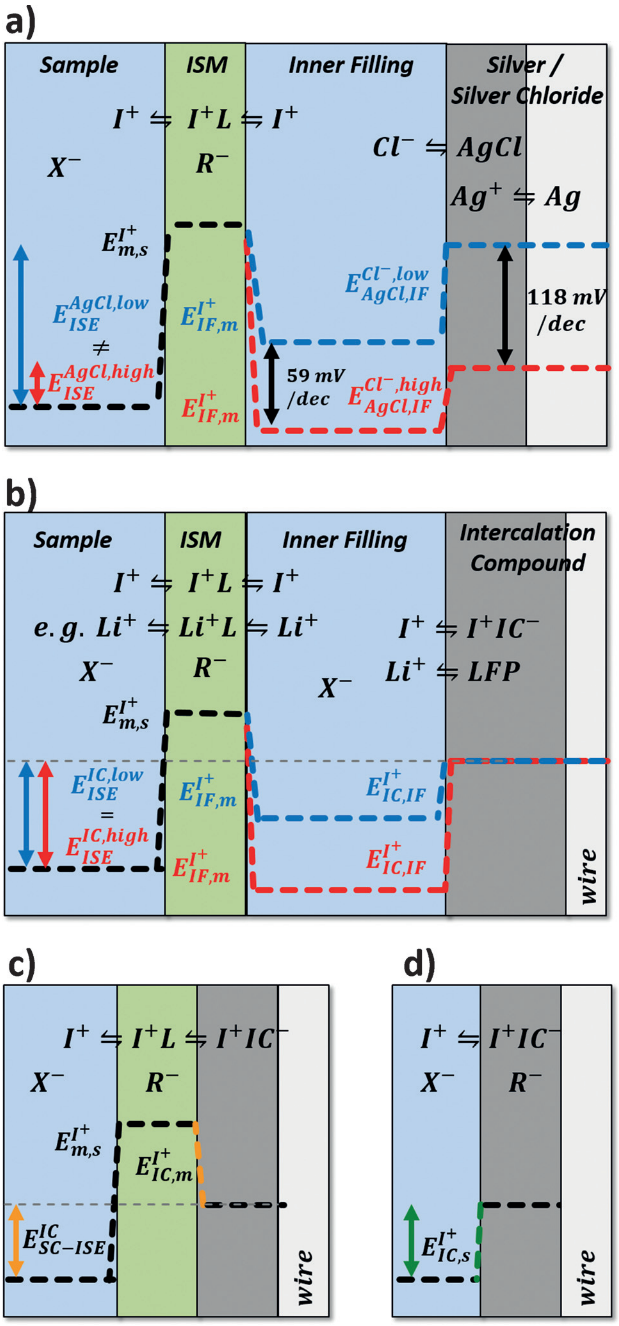

Figure 1. Illustration of electrochemical equilibria and potential distribution a) inside a classical IF-ISE for cations with Ag/AgCl iRE, and b) inside an IF-ISE with a cation-sensitive IC as iRE for high (red) and low (blue) concentrations of the inner filling solution; c) potential distribution inside a SC-ISE with an intercalation compound as solid contact; d) response of an intercalation compound in solution.

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[*] Y. Ishige
Center for Technology Innovation, Healthcare, Research & Development Group, Hitachi Ltd.
Higashi-Koigakubo 1–280, Kokubunji-shi, Tokyo, 185-8601 (Japan)
Dr. S. Klink, Prof. Dr. W. Schuhmann
Analytical Chemistry, Center for Electrochemical Sciences
Ruhr-University Bochum
Universitätsstrasse 150, 44780 Bochum (Germany)
E-mail: wolfgang.schuhmann@rub.de

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All three terms are defined by the activity of the chloride ions in the inner filling $a_{\mathrm{IF}}^{\mathrm{Cl}^-}$ and the activities of the target ion a_s^I, a_m^I, and a_{IF}^I in the sample solution, in the membrane and in the inner filling solution, respectively [Eq. (2)–(4)]:

$$E_{AgCl}^{Cl^-} = E_{AgCl,IF}^{0,Cl^-} - \frac{RT}{F}\boldsymbol{ln} a_{IF}^{Cl^-} \tag{2}$$

$$E_{IF,m}^{I} = +\frac{\mu^0(org) - \mu^0(aq)}{zF} - \frac{RT}{zF}\boldsymbol{ln}\frac{a_{IF}^I}{a_m^I} \tag{3}$$

$$E_{m,s}^{I} = -\frac{\mu^0(org) - \mu^0(aq)}{zF} + \frac{RT}{zF}\boldsymbol{ln}\frac{a_s^I}{a_m^I} \tag{4}$$

where $\mu^0(\mathrm{org})$ and $\mu^0(\mathrm{aq})$ are the standard chemical potentials of the membrane and the aqueous solution, R is the gas constant, z is the charge of the target ion, F is the Faraday constant, and T is the absolute temperature.

When Equations (2) to (4) are inserted in Equation (1), $\mu^0(\mathrm{org})$, $\mu^0(\mathrm{aq})$, and a_m^I are cancelled out. At any given inner filling with fixed concentration, $E_{\mathrm{ISE}}^{\mathrm{AgCl}}$ further simplifies to the Nernst equation for the ISE [Eq. (5)]:

$$E_{\mathrm{ISE}}^{\mathrm{AgCl}} = E_{\mathrm{ISE}}^{0,\mathrm{AgCl}} + \frac{RT}{zF}\boldsymbol{ln} a_s^I \tag{5}$$

with [Eq. (6)]

$$E_{\mathrm{ISE}}^{0,\mathrm{AgCl}} = E_{\mathrm{AgCl,IF}}^{0,\mathrm{Cl}^-} - \frac{RT}{F}\boldsymbol{ln} a_{\mathrm{IF}}^{Cl^-} - \frac{RT}{zF}\boldsymbol{ln} a_{\mathrm{IF}}^I \tag{6}$$

In the case of cation sensitive ISEs, the inner filling is key for the stability of the ISE potential since the constant activity of I^+ and Cl^- renders the response of the ISE solely dependent on the activity of I^+ in the sample solution.

The change from centralized analysis to point-of-care diagnostics, however, shifts the requirements from rugged macro-electrodes with a sufficiently large reservoir of inner filling towards small electrodes for integrated systems, which can be mass produced to reduce the cost of a single test. Hence, the volume of the inner filling has to be significantly decreased or ideally omitted while maintaining a predictable, reproducible, and stable standard potential. Decreasing the amount of inner filling may be achieved by confining the inner filling in a small volume hydrogel.[2] Hydrogel ISEs behave similarly to macroscopic IF-ISEs, their potential stability, however, is often compromised by the uptake of water and hydrogel swelling.[3] In the case of cation-sensitive ISEs, the difficulty is seen in the asymmetric response of $E_{\mathrm{AgCl,IF}}^{\mathrm{Cl}^-}$ (towards anions) and $E_{\mathrm{IF},m}^I$ (towards cations). Thus, $E_{\mathrm{ISE}}^{0,\mathrm{AgCl}}$ remains a function of $a_{\mathrm{IF}}^{I^+}$ and $a_{\mathrm{IF}}^{Cl^-}$, and $E_{\mathrm{ISE}}^{\mathrm{AgCl}}$ suffers from changes of the IF. Figure 1a illustrates this relationship. For example, changing the concentration of the inner filling by 10% alters $E_{\mathrm{ISE}}^{\mathrm{IF}}$ by 4.88 mV (118 mV/decade), which corresponds to an apparent error in target-ion concentration of 21%.

In so-called solid-contact ISEs (SC-ISEs) the inner filling is completely omitted. As a result, the interface potentials $E_{\mathrm{AgCl,IF}}^{\mathrm{Cl}^-}$ and $E_{\mathrm{IF},m}^I$ in Equation (1) are replaced by a new interface potential $E_{m,sc}^x$ between the ISM and the solid contact [Eq. (7)]:

$$E_{\mathrm{SC-ISE}} = E_{m,sc}^x + E_{s,m}^I \tag{7}$$

where x represents a species or set of species at the interface of the solid contact and the membrane.

For fluoride and chloride-selective SC-ISEs, the corresponding silver halogenides serve as a suitable inner reference. Fjeldly and Nagy demonstrated that the symmetric response of anion-selective glasses and corresponding metal salts towards the target anion results in anion-selective ISEs with well-defined potentials as, for example, Ag/AgF/LaF$_3$.[4]

Evidently, an alternative iRE is needed especially for cation-sensitive SC-ISEs, since [Cl$^-$] and $E_{\mathrm{ISE}}^{0,\mathrm{AgCl}}$ from Equation (6) are not clearly defined anymore. Several alternative iREs for both cation- and anion-sensitive SC-ISE have been suggested so far, including 1) large surface area carbons, 2) (potential-controlled) conducting polymers as solid contacts, or 2) the incorporation of hydrophobic redox couples into the ISM. Especially the first two groups can be utilized for both cation- as well as anion-sensitive ISEs.

In the case of solid carbon contacts, such as carbon blacks or carbon nanotubes, $E_{m,sc}^x$ is largely determined by the surface chemistry of the carbon.[5] The potential stability may be increased by increasing the interfacing surface area.[6,7] The capability to store charge, however, remains surface-confined with rather low capacitance and/or pseudo-capacitance and undefined total potential. Conducting polymers, such as polypyrrole[8] or PEDOT,[9] offer a higher redox capacity than carbon since the target ions can be inserted in the polymer upon reduction of the polymer backbone. Nevertheless, conducting polymers are characterized by a wide range of redox potentials which renders the prediction and long-term stability of the standard potential difficult. More sophisticated approaches need to be applied to control the absolute potential.[10] Another approach is adding a hydrophobic redox couple as a “redox buffer” into the ISM, resulting in quite remarkable initial reproducibility.[11,12] Nevertheless, this approach requires the composition of the ISM to be altered. Potentials drift by several tens of millivolts over just a few hours after immersion in electrolyte were observed.

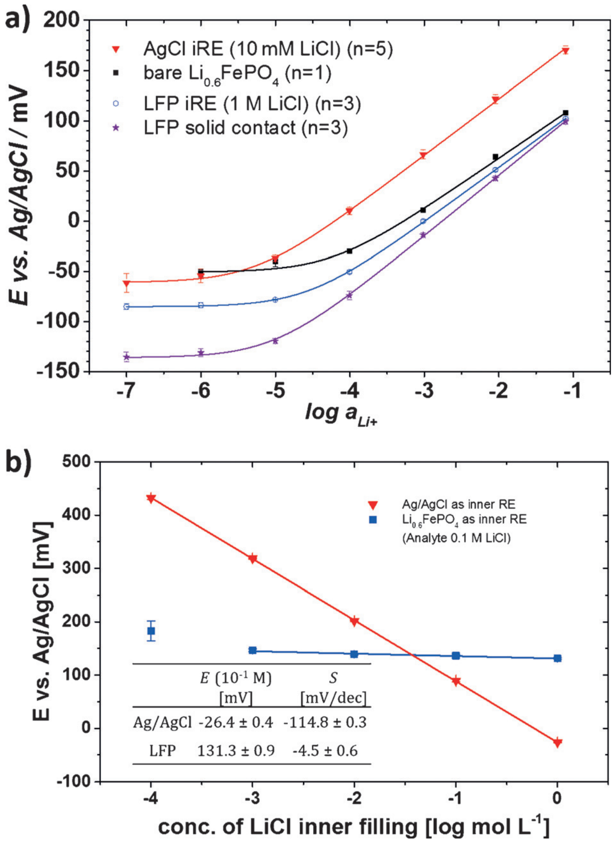
Thus, the dilemma lies in compromising either simplicity (i.e. cost of material or production) or robustness (i.e. predictability, reproducibility and/or stability of the sensor) when moving from macroscopic IF-ISEs to microscopic IF-ISEs or SC-ISEs. To be more specific, the challenge is to find a non-polarizable ion-to-electron transducer with defined potential and high redox capacitance which neither depends on the composition of the inner filling nor on the membrane.[2,13] From Equation (5), however, the solution to this dilemma is actually simple. If the iRE responds to target cations directly rather than to chloride ions, the terms in Equation (5) are cancelled out and the ISE becomes insensitive to changes of the inner filling. Intercalation compounds (ICs) show a Nernstian response towards the activity of cations,[14,15] and therefore seem to be ideal for this purpose. As illustrated in Figure 1bthe standard potential of an ISE with an iRE based on a target-ion intercalating compound $E_{\mathrm{ISE}}^{0,\mathrm{IC}}$ is solely determined by the standard potential of the iRE $E_{\mathrm{IC}}^{0,I}$ [Eq. (8)]:

$$E_{\mathrm{ISE}}^{0,\mathrm{IC}} = E_{\mathrm{IC}}^{0,I} + \frac{RT}{zF}\boldsymbol{ln} a_{\mathrm{IF}}^{I} - \frac{RT}{zF}\boldsymbol{ln} a_{\mathrm{IF}}^{I} = E_{\mathrm{IC}}^{0,I} \qquad (8)$$

LiFePO$_4$ (LFP), for example, a well investigated material in lithium-ion batteries, can reversibly intercalate and de-intercalate Li$^+$ ions upon electrochemical reduction and oxidation of the Fe$^{II/III}$ redox centers.[16] The intercalation proceeds as two-phase reaction with a very flat potential plateau over a wide range of Li content (ca. 170 mAh g^{-1}) as governed by the Gibbs phase rule.[17] This offers the advantage of a very well defined redox potential as well as a huge redox capacity with low polarization for high stability. Owing to these properties, partially lithiated LFP electrodes can be used as reference electrodes[18] or potentiometric sensors for Li$^+$ in aqueous solution,[14,15] but both sensitivity and selectivity towards other alkali ions is too low for a meaningful application.

In the case of SC-ISE, $E_{\mathrm{SC-ISE}}^{0,\mathrm{IC}}$ can be similarly defined, as long as the potential between ISM and solid contact $E_{m,sc}^{x}$ is dominated by the target cation (see Figure 1 c). IC-based ISEs were first presented by Komaba et al.,[19] exhibiting a potential stability of ±5 mV for 15 days. However, the electrodes required individual electrochemical conditioning and the absolute value and reproducibility of the standard potential was not reported.

According to Lindner and Gjurcsányi's summary on quality criteria for SC-ISEs, adequate SC are identified by the reproducibility of the standard potential rather than the long-term stability of a single electrode.[4] We therefore revisited the use of partially lithiated LFP electrodes in order to develop IF-ISE with a defined and reproducible standard potential. Figure 2 a shows the sensitivity and selectivity of the LFP-based IF-ISE which are governed by the ISM and are hence similar to those of classical Ag/AgCl based IF-ISEs. As illustrated in Figure 2 b, the potential of the LFP-based IF-ISE is nearly insensitive to changes of the inner filling within a range of more than three orders of magnitude, as expected from Equation (8). While classical Ag/AgCl electrodes exhibit a strong linear dependence of 115 mV per decade of LiCl concentration owing to the twofold sensitivity to [Cl$^-$] as described in Equation (6), $E_{\mathrm{IC}}^{0,I}$ differs by less than 5 mV/decade of LiCl concentration. This property actually describes a surprisingly simple solution to the inherent stability issues of IF-ISE arising from water-uptake (or dry-out), especially in small volumes such as in hydrogel-based IF-ISEs.



	E (10^{-1} M) [mV]	*S* [mV/dec]
Ag/AgCl	-26.4 ± 0.4	-114.8 ± 0.3
LFP	131.3 ± 0.9	-4.5 ± 0.6

Figure 2. a) Potential response curve of five classical Li-ISEs with Ag/AgCl (10^{-2} M LiCl) as iRE; a bare LFP-coated wire, three Li-ISEs with LFP (1 M LiCl) as iRE, and three SC-ISEs with LFP as solid contact. Error bars and lines represent standard deviations and fitting curves (see Supporting Information); b) Influence of the inner filling concentration in the case of Li-ISE with Ag/AgCl and LFP iRE.

Motivated by these results, we further investigated the preparation of LFP-based SC-ISEs. Chemical oxidation of LFP by means of NO$_2$BF$_4$ prior to electrode preparation is a means of charge control which avoids any electrochemical treatment of the assembled electrode and hence opening the route to facile mass production. Moreover, we avoided the use of high surface area carbon blacks as conductive additive and limited the surface area by compression. Such electrodes with a thickness of about 20 μm provided a nominal redox capacity of roughly 0.1 As per electrode as measured by charge/discharge cycling. ISMs were then directly glued or solution-cast onto the solid contacts (Supporting Information; Figures S1–S3). Reproducible ISEs with initial potentials of 98.7 ± 1.4 mV in 10^{-1} mM LiCl (vs. Ag/AgCl in 1 M KCl, $n = 9$) were obtained. These values are due to the Fe^{2+}/Fe^{3+} redox couple. Bare LFP electrodes show a potential of 100.7 mV under the same conditions. The reproducibility was comparable to that of Ag/AgCl based IF-ISE (230.5 ± 0.6 mV; $n = 4$) as well as superior to the best values reported for SC-ISE so far (±0.8 mV for redox-buffered ISEs[12]).

Alternatively, LFP can also be oxidized by H$_2$O$_2$ for charge control despite the stoichiometric reaction being more difficult to control. In this case, fully oxidized "Li$_0$FePO$_4$" is mixed with pristine LFP to yield Li$_{0.5}$FePO$_4$ electrodes with a potential of 99.3 ± 2.4 mV ($n = 3$) under the same conditions. SC-ISEs based on LFP showed Nernstian response (60.4 ± 0.8 mV/dec) down to the limit of detection (LoD) of 10$^{-5.0}$ M activity with selectivity coefficients of 10$^{-2.1}$ and 10$^{-2.0}$ against Na$^+$ and K$^+$, respectively. The slope of the response curve, the lower LoD and the higher selectivity compared to the bare LFP electrode (see Table 1) indicate that the assembly of LFP-based iRE and ISM rather than the bare LFP responded to Li$^+$ ions. The LoD was even smaller than that of the conventional IF-ISE with 10^{-2} M LiCl as inner filling. The reason may be a decreased ion flux from the membrane, a characteristic which was anticipated but not frequently observed for SC-ISE.[4,20]

Table 1: Response properties of SC-ISE and IF-ISE with LFP as iRE and solid contact and those of classical ISE with Ag/AgCl as iRE.

Redox couple	Ag/AgCl IF-ISE 10^{-2} M LiCl	LFP[a] Bare	LFP[b] IF-ISE 1 M LiCl	LFP[b] IF-ISE 10^{-4} M LiCl	LFP[a] SC-ISE
E (1 d) [mV] (10^{-1} M LiCl)	162.3 ± 0.5 ($n = 4$)	100.7 ($n = 1$)	102.0 ± 1.6 ($n = 3$)	154.1 ± 18 ($n = 3$)	98.7 ± 1.4 ($n = 9$)
E (42 d) [mV]	156.4 ± 2.9	n/a	–	–	97.0 ± 1.5
Stability [$\mu V h^{-1}$]	-8.1 ± 2.6	n/a	–	–	-1.1 ± 1.4
E^0 [mV] ($\log a = 0$)	230.5 ± 0.6 ($n = 4$)	159.2 ± 6.5	162.4 ± 1.1	217.9 ± 2.5	166.4 ± 2.0 ($n = 3$)
S [$mV dec^{-1}$]	58.7 ± 0.3	54.6 ± 3.2	54.5 ± 0.4	56.6 ± 0.9	60.4 ± 0.8
$\log a_{LOD}$	-4.55 ± 0.04	-3.76 ± 0.13	-4.55 ± 0.03	-4.95 ± 0.05	-5.01 ± 0.06
$\log K^{pot}_{Li,Na}$	-2.20[c]	n/a	n/a	-2.19[c,e]	-2.1[b,d]
$\log K^{pot}_{Li,K}$	-2.03[c]	n/a	n/a	-1.99[c,e]	-2.0[b,d]

[a] Chemically oxidized. [b] Electrochemically oxidized. [c] By the fixed interference method, 0.1 M KCl, NaCl. [d] By the separate solution method. [e] Data for 10^{-2} M LiCl inner filling (IF).

Evaluating the potential stability provides information on how well-defined the interface between a solid contact and an ISM is.[4,9] Previous publications reported SC-ISEs with potential stabilities of 1.3 μV h^{-1}, 11.7 μV h^{-1}, or 30 μV h^{-1} over the course of 3 days for colloid-imprinted mesoporous carbon,[7] three-dimensionally ordered macroporous carbon,[6] and conducting polymers[21] used as solid contact, respectively.

In our experiments, LFP-SC-ISEs exhibited high stability with no statistically significant potential drift (-1.1 ± 1.4 μV h^{-1}) over a much longer course of 42 days when inserted into the analyte solution. While the variance of the electrode potential over this time was around 3.5 mV measured versus an outer reference electrode (see Figure 3), the ISEs did not only preserve their narrow potential distribution (97.0 ± 1.5 mV on the 42nd day), but also kept their individual potential offset with respect to the average potential of the whole set within a standard deviation of as little as 0.7 mV. This value as well as a qualitative assessment of the course of the electrode potentials gives a strong indication that the observed long-term variance of the total potential was actually influenced by parameters, such as temperature or stability of the outer reference electrode, rather than due to a potential drift of the ISEs. The SC-ISEs could even be stored in dry conditions for more than 5 months and quickly restored their potential in analyte solution to 94.5 ± 2.7 mV, that is, a decrease of less than 3 mV.

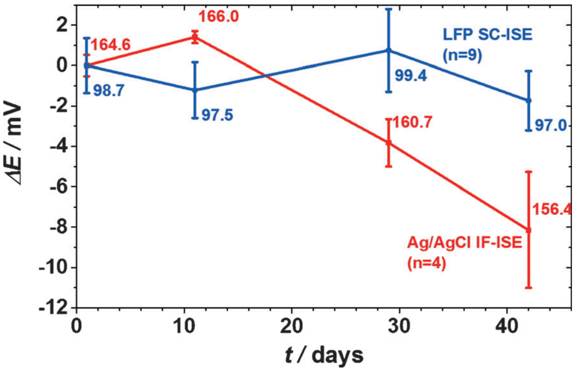


Figure 3. Long-term potential drift and reproducibility (as error bars) of four Ag/AgCl IF-ISEs and nine LFP-SC-ISEs over 42 days. Potentials were measured in 10^{-1} M LiCl, which was freshly prepared for each measurement. Labels indicate the average of absolute potentials vs. Ag/AgCl (1 M KCl).

Similar information is also (and much faster) obtained from constant current polarization experiments, simulated deterioration of the ISM and so-called water-layer tests[4,9a,22] as accelerated aging test (see Supporting Information).

Cation-sensitive intercalation compounds can be used as inner reference electrodes of pseudo-first kind for cation-sensitive ISEs. These ISEs can be easily miniaturized and produced on a large scale using conventional chemical processing and screen-printing techniques, since they do not require an inner filling of any kind. As one example, an SC-ISE based on the $LiFePO_4/FePO_4$ redox couple showed a well-defined standard potential of 97.0 mV with high electrode to electrode reproducibility (±1.5 mV), no significant potential drift over several weeks and an average standard deviation of each electrode from its individual potential offset as little as ±0.7 mV. In combination with a matrix-independent reference system such as the ferrocene/ferricenium couple,[23] it may even be possible to create a fully "dry" two-electrode analytical system.

The promising results shown for $LiFePO_4/FePO_4$ based ISEs raise the question if more intercalation compounds can be identified which intercalate other cations, such as Na^+, K^+, Ca^{2+}, or Mg^{2+}, or even anions for the development of corresponding ISEs. Exploring the growing family of intercalation materials in battery research, such as oxides or phosphates, would be a good starting point.

Experimental Section

Reference electrodes: Ag/AgCl iREs were prepared by chloridizing silver wires (Goodfellow) in 0.1 M HCl/3 M KCl. LFP iREs were prepared by dispersing battery grade LFP (MTI) with SFG6 graphite (Timcal) in a PVdF (polyvinylidene difluoride) solution (Solef S5130, Solvay) in NMP (*N*-methyl pyrrolidone) (Sigma–Aldrich) and coating the slurry on a 0.5 mm Pt wire (Goodfellow). After drying at 60 °C, the electrode coating had a composition of LFP:SFG6:PVdF of 80:12:8 wt %. These electrodes were electrochemically delithiated. For SC-ISE, an 85:10:5 slurry of chemically oxidized LFP (see Supporting Information) was coated on a graphite foil. 6 mm discs were punched out and compressed at 10^5 N cm^{-2}.

Ion-selective membranes: 100 mg PVC (high molecular, Fluka), 200 mg 1-(2-nitrophenoxy)octane (NPOE, Fluka), 3 mg 6,6-dibenzyl-14-crown-4 (Li-ionophore VI, 99 %, Sigma–Aldrich), and 2 mg potassium tetrakis(4-chlorophenyl)borate (KTpClPB, 98 %, Sigma–Aldrich) were dissolved in 3 mL tetrahydrofuran (THF, 99.9 %, inhibitor-free, Sigma–Aldrich). The solution was poured into a 34 mm petri dish and allowed to dry. The resulting membrane was punched into discs and soaked overnight in 10^{-2} M LiCl for ion exchange. For IF-ISE, the membranes were glued onto 8 mm × 8 cm hard PVC U-tubes using THF. The tube was filled with the IF and equipped with either Ag/AgCl or LFP iRE and soaked overnight. For SC-ISE, the membranes were glued on the compressed LFP or graphite foil electrodes. The resulting assembly was then mounted on a PTFE-embedded glassy carbon electrode and fixed by a PEEK cap nut (see Supporting Information).

Electrochemistry: Experiments were carried out in a standard glass cell equipped with the ISE of choice and a Ag/AgCl RE with single junction (Metrohm) or double-junction with 10^{-2} or 10^{-1} M LiCl or 1 M KNO_3 outer filling (Orio 900200 Sure-Flo, Thermo Scientific). A Bio-Logic VMP-3 potentiostat (BioLogic) was used. All potentials are reported vs. the Orion RE, which corresponds to a Ag/AgCl (1 M KCl) electrode. For chronopotentiometry, a Pt-net counter electrode was used. Selectivity coefficients were determined by the fixed interfering ion method or separate solution method with a concentration of sodium and potassium as interfering ion of 10^{-1} M Response curves including LODs, slopes and standard potentials were reported by calculating activity coefficients based on the Debye–Hückel approximation as reported by Meier.[24] Fresh solutions were used before taking data points.

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Keywords: cation intercalation compounds · inner reference electrode · ion-selective electrodes · lithium iron phosphate · solid contact

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