Electronic Supplementary Material (ESI) for Analytical Methods.

Supporting information

Single strip solid contact ion selective electrodes on pencil-drawn electrode substrate

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Abstract

Herein, we include more detailed information associated with the study on long-term stability of NH_4^+ - selective electrodes.

Results and discussion

Table S1. Selectivity coefficients for selected ions obtained for NH_4^+ - selective electrode using acetate sheet/graphite – based substrate and traditional membrane composition.

Ion	logK potij ± S.D	Slope ± S.D
Na^+	-2.96 ± 0.03	57.53 ± 0.27
Cs^+	-2.56 ± 0.03	54.05 ± 0.06
K^+	-0.98 ± 0.02	55.24 ± 0.15
NH_4^+	0	56.35 ± 0.30

Table S2. Selectivity coefficients for selected ions obtained for NO_3^- - selective electrode using acetate sheet/graphite – based substrate and traditional membrane composition.

Ion	logK potij ± S.D	Slope ± S.D
Cl^-	-2.48 ± 0.02	-52.93 ± 0.30
NO_2^-	-1.27 ± 0.03	-53.57 ± 0.54
I^-	1.4 ± 0.03	-55.24 ± 0.15
CLO_4^-	3.25 ± 0.02	-54.35 ± 0.25
NO_3^-	0	-55.78 ± 0.21

Long-term stability

Enclosed are graphs of six additional electrodes used in the long term stability study (Figure S1). As per discussion in the main text, electrodes were conditioned according to the following protocol:

Prior the first use electrodes were conditioned overnight 1.0 x 10^{-3} M NH_4Cl solution and stored in air. Electrodes were rehydrated in the same solution for 1 hour prior to subsequent calibration.

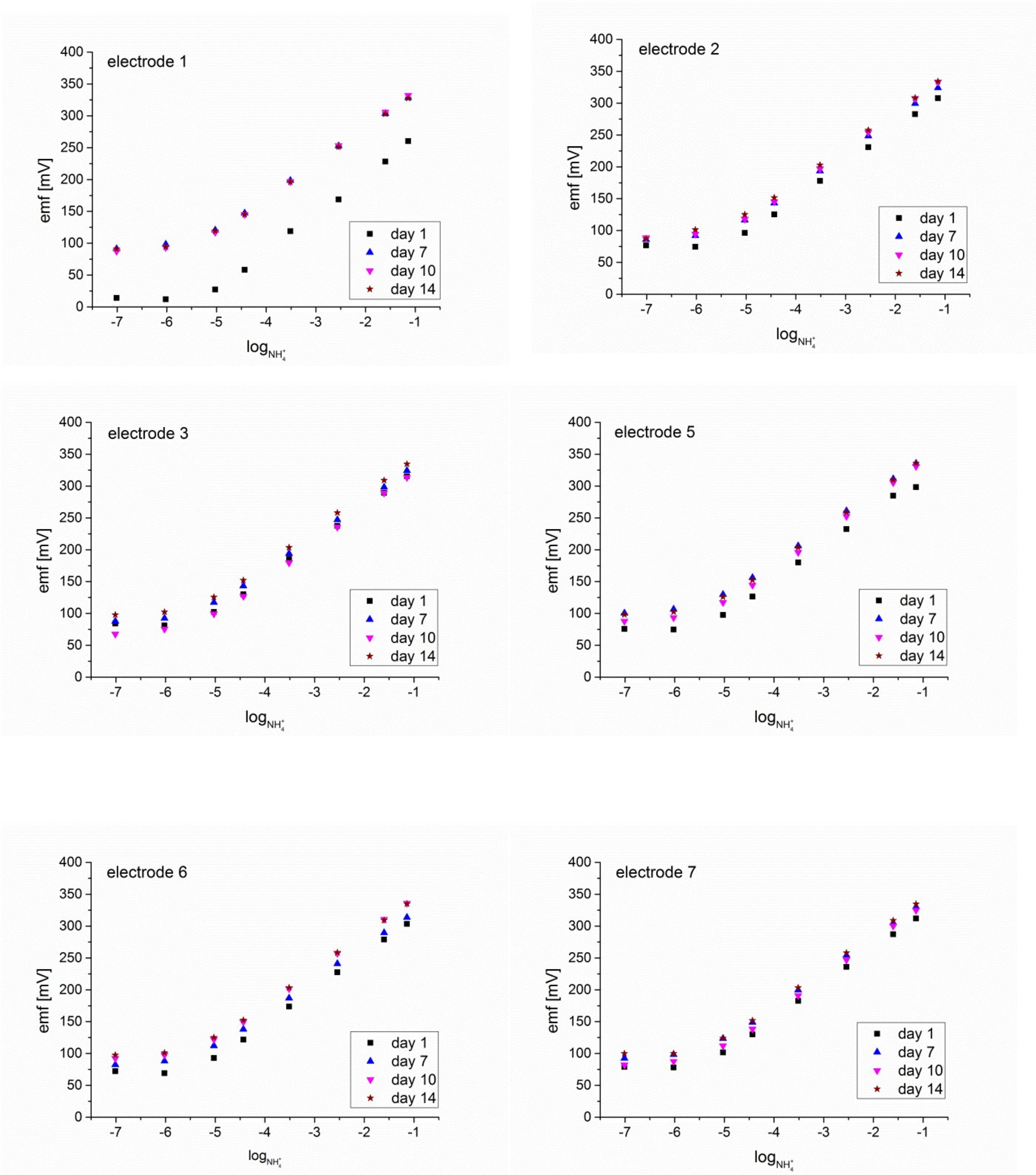


Figure S1. Potentiometric responses of ISEs used for the long term stability study.

Table S3. E^0 and base line potential averaged over time.

Electrode	E^0	Base line
1	376.18 ± 34.13	71.0 ± 38.03
2	388.21 ± 13.05	84.6 ± 5.44
3	384.98 ± 9.26	84.3 ± 12.47
4	383.59 ± 4.05	83.6 ± 6.26
5	388.8 ± 18.28	90.5 ± 11.28
6	385.01 ± 17.14	86.1 ± 11.2
7	388.76 ± 10.13	88.4 ± 9.66

As observed, E^0 and base line is surprisingly stable especially considering the incredibly simple protocol for electrode preparation. No training is necessary and platforms are prepared using typical household materials. Interestingly, major source of instability originates from the response during the first day. In fact, excluding electrode 1, average E^0 across all electrodes and all days is 386±15 mV while base line potential is 86±11 mV. Further studies in the origins of the noticed slight instability can result in protocols for preparation of sensors on a truly mass scale at very low cost.

Characterization of all-solid-contact reference electrode

A reference electrode is an essential tool in potentiometry because it functions as a fixed constant that completes an electrochemical cell. The potential of a reference electrode should ideally be insensitive to any changes occurring in the background solution and should maintain constant and stable potential throughout the measurement. Therefore, we investigated whether the proposed substrate (modified acetate sheet with mechanically deposited graphite) could be used for the development of functional potentiometric sensing devices. For that purpose, solid-contact reference electrodes based on the highly lipophilic tetrabutylammonium tetrabutylborate (TBA-TBB) salt were fabricated and prepared as explained in the experimental section. They were characterized against a classical glass double-junction reference electrode (Fluka) to investigate potential stability due to change in electrolyte concentration. Characterization was based on slightly modified protocol developed by Mattinen et al.[1] Table S4 shows details of employed protocol while Figure S2 illustrates potential response of the two types of electrodes.

Table S4. Protocol for investigating potential stability of solid-contact TBA-TBB – based reference electrode on graphite-based substrate

Protocol	Solution concentration	Time/ min
I	0.1 M KCl	10
	0.01 M KCl	10
	0.1 M KCl	10
	0.01 M KCl	10
II	0.1 M KCl	10
	0.0001 M KCl	10
	0.0001 M NaCl	10
	0.1 M NaCl	10
	0.1 M KCl	10
III	0.01 M KCl	0.5
	0.1 M KCl	0.5
	0.01 M KCl	0.5

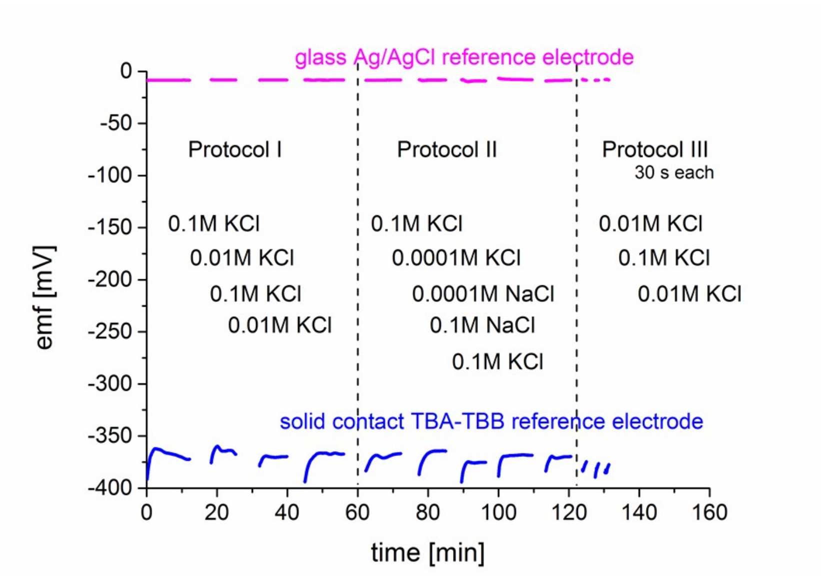
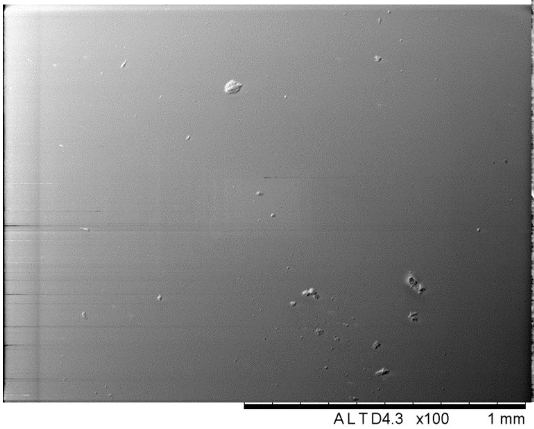


Figure S2. Potential behavior of the reference electrode based on TBA-TBB on graphite substrate compared to a conventional glass double-junction reference electrode.

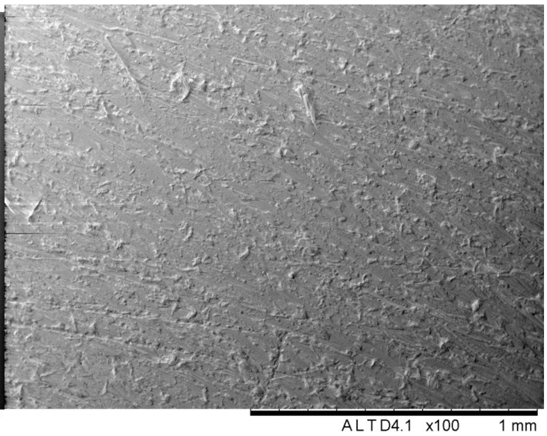
A relatively slow response of TBA-TBB – based reference electrodes has also been observed in the original work by Mattinen et al.[1] Clearly, applications that require fast measurements will be impeded; however, excellent stability of the signal after equilibration is very encouraging for development of ultra-cheap sensing devices for majority of applications.

SEM and EDS

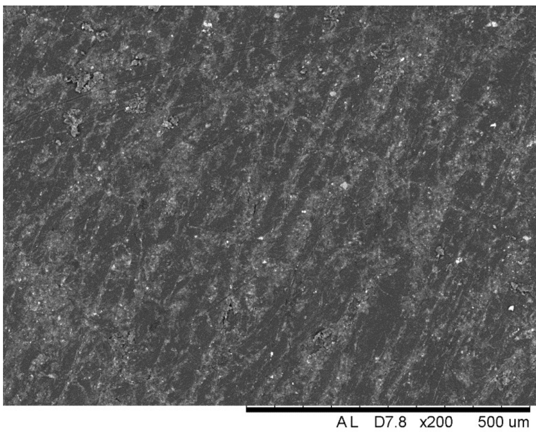
SEM (Hitachi TM3000) that includes EDS was used to investigate surphase morphology and elemental analysis of various graphite pencils contained in the box called Artist's Pencils ranging from 4H to 4B (hardest to softest respectivley).



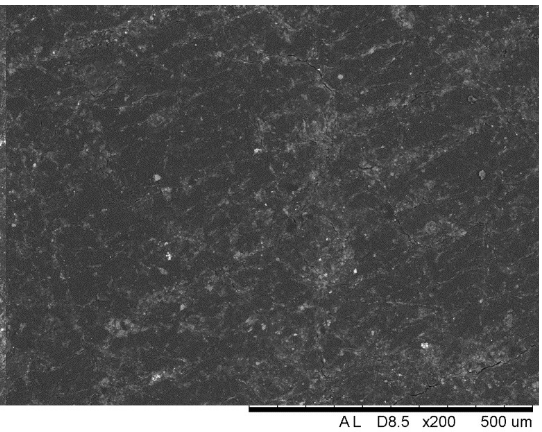
Acetate paper



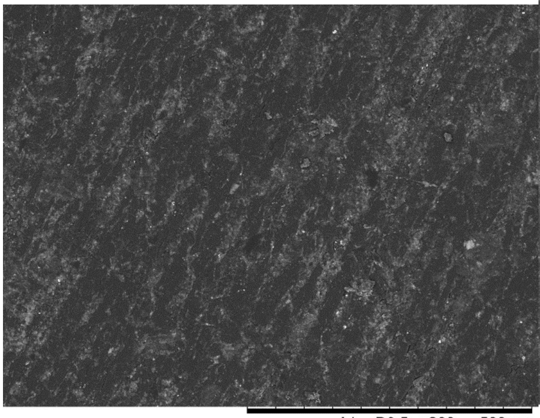
Roughened acetate paper



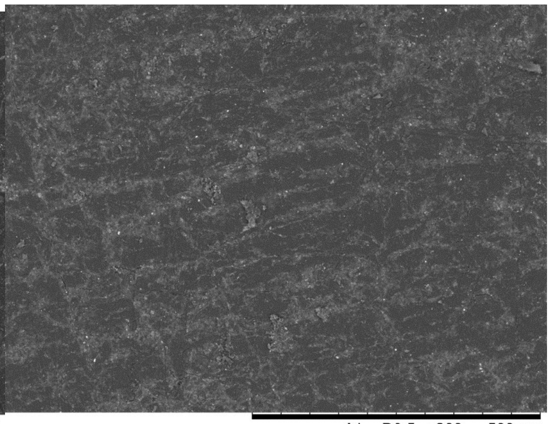
4B



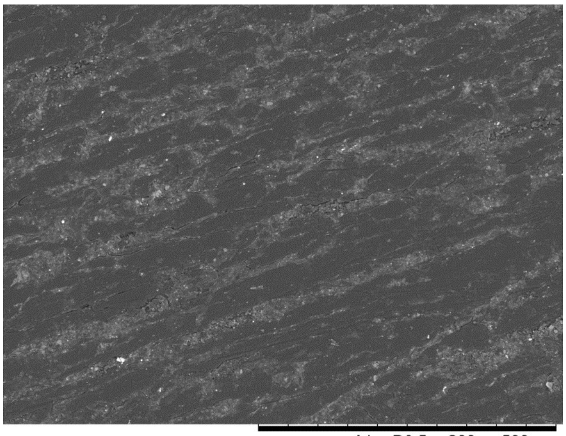
2B



HB



2H



4H

References

1 U. Mattinen, J. Bobacka and A. Lewenstam, *Electroanalysis*, 2009, **21**, 1955–1960.