



Electrolyte engineering toward efficient water splitting at mild pH

Item Type	Article
Authors	Shinagawa, Tatsuya;Ng, Marcus Tze-Kiat;Takanabe, Kazuhiro
Citation	Shinagawa T, Ng MT-K, Takanabe K (2017) Electrolyte engineering toward efficient water splitting at mild pH. ChemSusChem. Available: http://dx.doi.org/10.1002/cssc.201701266 .
Eprint version	Post-print
DOI	10.1002/cssc.201701266
Publisher	Wiley
Journal	ChemSusChem
Rights	This is the peer reviewed version of the following article: Electrolyte engineering toward efficient water splitting at mild pH, which has been published in final form at http://doi.org/10.1002/cssc.201701266 . This article may be used for non-commercial purposes in accordance With Wiley Terms and Conditions for self-archiving.
Download date	2024-04-16 09:36:04
Link to Item	http://hdl.handle.net/10754/625422

Supporting Information

Electrolyte engineering toward efficient water splitting at mild pH

Tatsuya Shinagawa, Marcus Tze-Kiat Ng, and Kazuhiro Takanabe*

King Abdullah University of Science and Technology (KAUST), KAUST Catalysis Center (KCC) and
Physical Sciences and Engineering Division (PSE), 4700 KAUST, Thuwal, 23955-6900 (Saudi Arabia)

E-mail: kazuhiro.takanabe@kaust.edu.sa

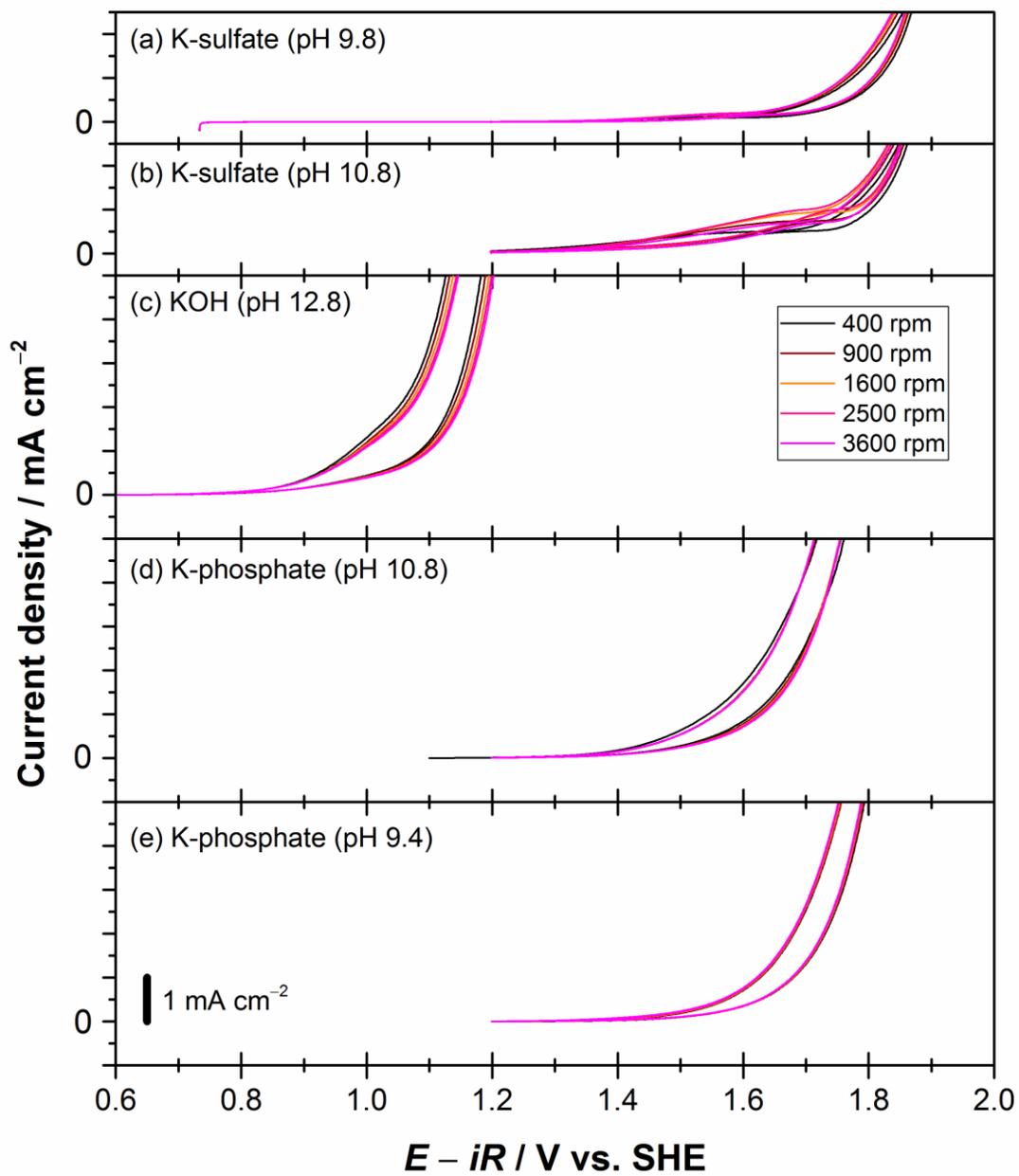


Figure S1. CVs using a Pt RDE in (a) 0.1 M K-sulfate (pH 9.8), (b) 0.1 M K-sulfate (pH 10.8), (c) 0.1 M KOH (pH 12.8), (d) 0.1 M K-phosphate (pH 10.8), and (e) 0.1 M K-phosphate (pH 9.4) at 298 K at various disk-rotation speeds (400-3600 rpm) and a scan rate of 10 mV s⁻¹.

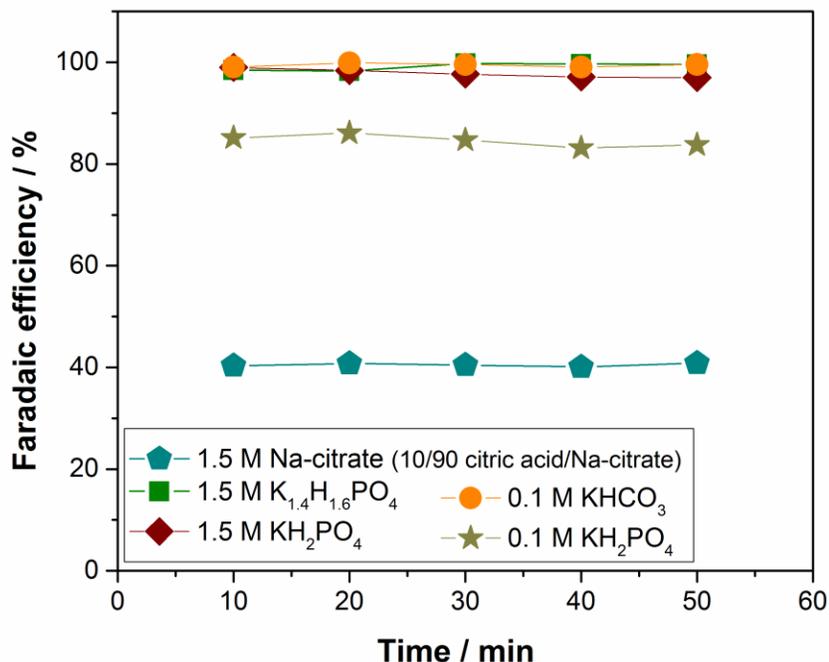


Figure S2. Faradaic efficiency for the oxygen evolution reaction as a function of time over 50 min in various electrolytes: 1.5 M (KH_2PO_4 , $K_{1.4}H_{1.6}PO_4$, $Na_{0.3}C_6H_7O_7$) and 0.1 M ($KHCO_3$, KH_2PO_4). All the measurements were carried out at 10 mA using a Ni plate ($1 \times 1 \text{ cm}^2$) electrode at 298 K.

In most solutions, the Faradaic efficiency for OER during CP was nearly 100%, indicating that the measured anodic current-potential relationship reflects OER. Notably, the Faradaic efficiencies for OER in mildly acidic solution (KH_2PO_4 ; pH ~ 4) and Na-citrate at pH 6.5 were not 100%. In some literature, the OER performance was reported without the quantification of products; however, the result shown here clearly suggests that, when OER is studied at near-neutral pH levels in buffered solution, the Faradaic efficiency must be examined to ensure that the current-potential relationship originates from OER.

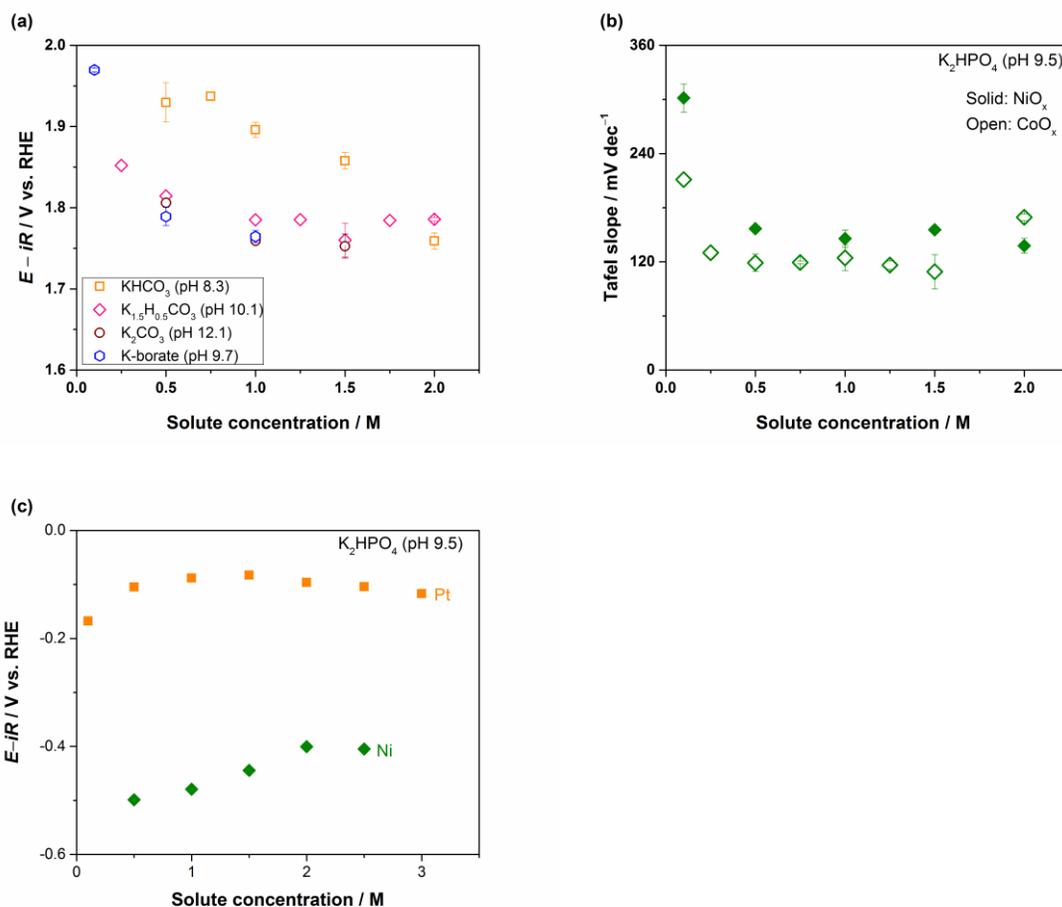


Figure S3. (a) Potential reaching 10 mA using a CoO_x plate in KHCO_3 (pH ~8.3), $\text{K}_{1.5}\text{H}_{0.5}\text{CO}_3$ (pH ~10.5), K_2CO_3 (pH ~12.1), and K-borate (pH 9.7); (b) Tafel slope using Ni and Co plates ($1 \times 1 \text{ cm}^2$) in K_2HPO_4 ; (c) potential reaching -10 mA cm^{-2} using Pt and Ni RDEs at 3600 rpm in K_2HPO_4 , adopted from reference.^[S1] All the figures are plotted as a function of the solute concentration.

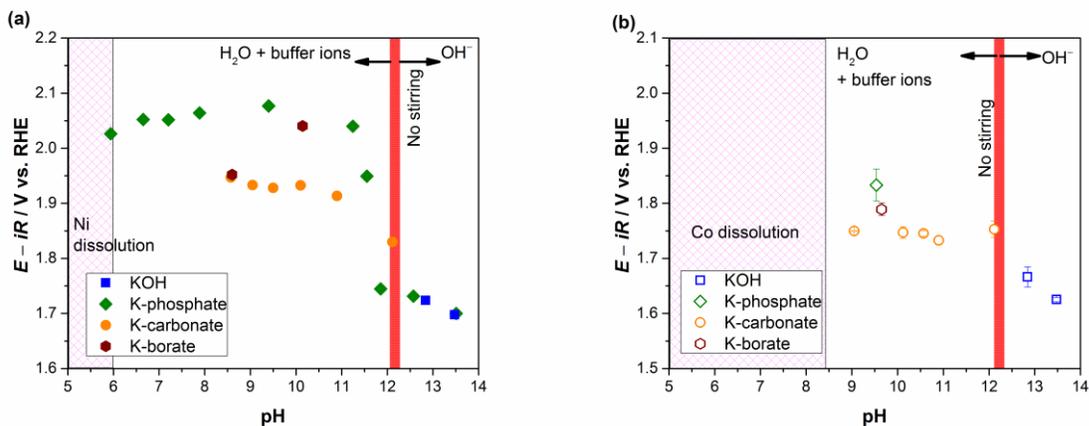


Figure S4. Potentials reaching 10 mA on the RHE scale plotted as a function of the solution pH in various electrolytes: 1.5 M $K_xH_{3-x}PO_4$ ($x = 1.2\sim 3.0$), $K_xH_{2-x}CO_3$ ($x = 1.0\sim 2.0$), 0.2 M K-borate (pH 8.6), 0.5 M K-borate (pH 9.7 & 10.1), and 0.1 M and 0.5 M KOH. The measurements were performed using (a) NiO_x and (b) CoO_x plate electrodes ($1\times 1\text{ cm}^2$) at 298 K. The potential-current relationships were obtained from CAs.

Above a pH of ca. 12 and at pH 4-10, the potentials required to reach 10 mA on the SHE scale shifted linearly with a changing pH. Nearly identical OER overpotentials were observed in KOH and K-phosphate at $pH \geq 12$ for NiO_x , which most likely originated from the electrolyte pH being higher than the isoelectric point of NiO_x (~ 11), consistent with previous literature.^[S2] In the figure, when the OER performances in various electrolytes were compared at similar pH levels (~ 9), the following order for the OER performance was obtained: carbonate > borate > phosphate.

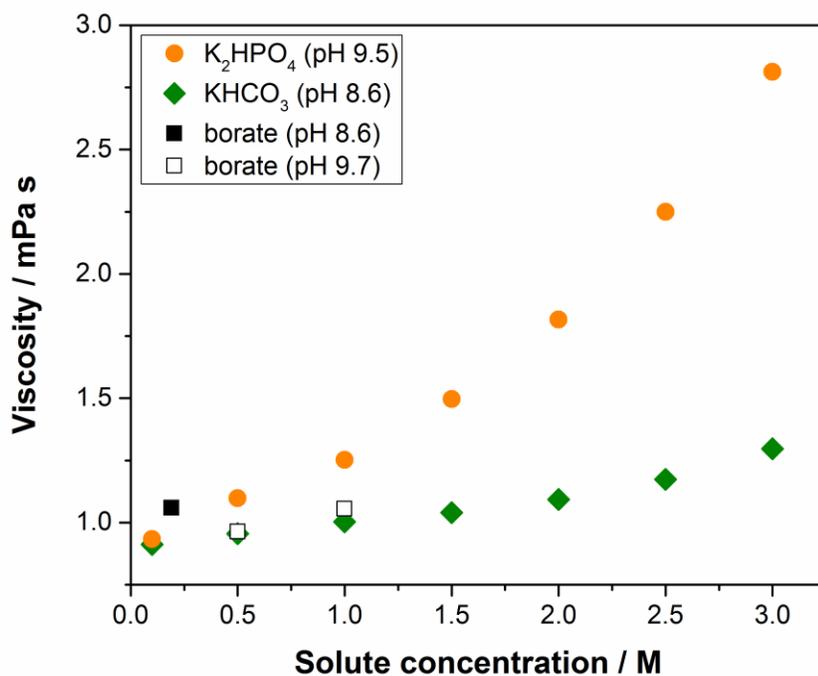


Figure S5. Viscosities of K₂HPO₄, KHCO₃, and K-borate as a function of the solute concentration, measured using a viscometer.

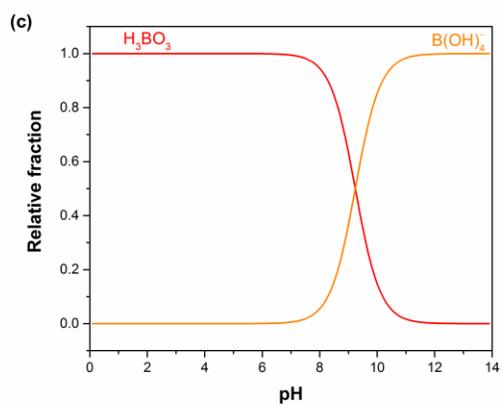
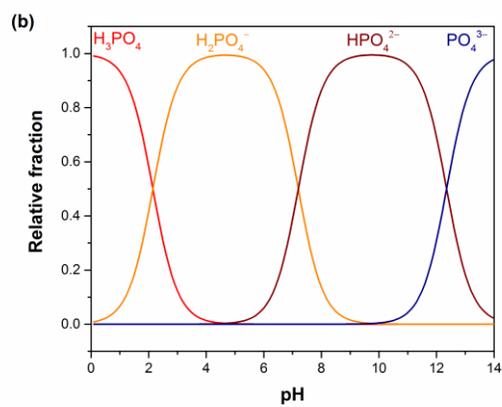
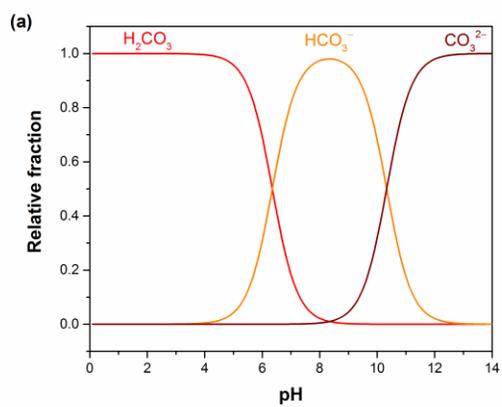


Figure S6. Relative fragments of species in (a) carbonate, (b) phosphate and (c) borate electrolytes as a function of the solute concentration, calculated with pKa values provided in the literature.^[S3,S4]

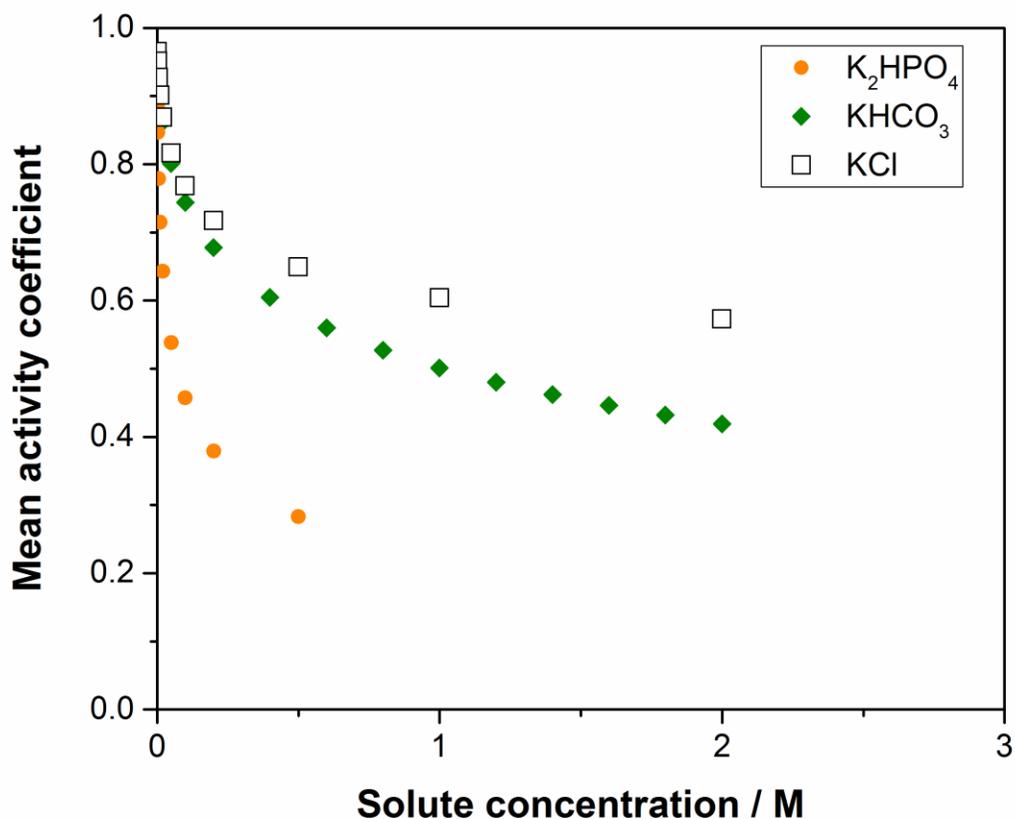


Figure S7. Mean activity coefficients for K_2HPO_4 , KHCO_3 and KCl as a function of the solute concentration using values adopted from literature.^[S3,S4]

The primary parameters that determine the mass-transport flux are the viscosity of solution, the size of species (in a hydrated form), the activity coefficient and the molarity of species in solution. These parameters are simple characteristics of each electrolyte, which can be separately examined. The viscosities of KHCO_3 , K_2HPO_4 and K-borate were measured using a viscometer and are presented in Figure S5. The size of HCO_3^- is reported to be in the range of 0.4~0.45 nm, that of HPO_4^{2-} is ca. 0.4 nm, and K^+ is approximately 0.3 nm.^[S5] Although the size of $\text{B}(\text{OH})_4^-$ has not been explicitly determined in the literature to the best of our knowledge, considering its structure and charge, it would be reasonable to

anticipate that its size is similar to or slightly larger than that of HCO_3^- . With the obtained viscosities and sizes, the diffusion coefficients of these species were calculated using the Stokes-Einstein equation^[S5] and are compiled in Figure 5 of the main manuscript. The activities of the ions in solution are described as the molarities multiplied by the mean activity coefficients. In this study, to examine the OER performance and electrolyte properties at a similar pH value, the pH of K-borate was adjusted to 9.7 by adding H_3BO_3 . Therefore, to accurately describe the activity of $\text{B}(\text{OH})_4^-$ in the K-borate solution at pH 9.7, the relative fraction of $\text{B}(\text{OH})_4^-$ needs to be determined. The relative fraction is readily calculated from the pKa values, and the calculated values are summarized in Figure S6. Regarding the mean activity coefficient, the data for $\text{K}^+\text{-HCO}_3^-$ and $\text{K}^+\text{-HPO}_4^{2-}$ are available in the literature,^[S3] while that of $\text{K}^+\text{-B}(\text{OH})_4^-$ has not been explicitly determined. Nevertheless, according to the literature, the mean activity coefficient for $\text{K}^+\text{-B}(\text{OH})_4^-$ was reported to be similar to that of KCl .^[S7] Figure S7 compiles the mean activity coefficients for $\text{K}^+\text{-HCO}_3^-$, $\text{K}^+\text{-HPO}_4^{2-}$ and $\text{K}^+\text{-Cl}^-$. Please note that the presence of other species (H_3BO_3 in this case) can change the activity coefficient of the species of interest ($\text{B}(\text{OH})_4^-$ in this case), and thus, the use of the value of the mean activity coefficient for further discussions regarding K-borate is ambiguous to some extent. With the values in Figure S7, the activities of HCO_3^- and HPO_4^{2-} were calculated and are presented in Figure 5 of the main manuscript.

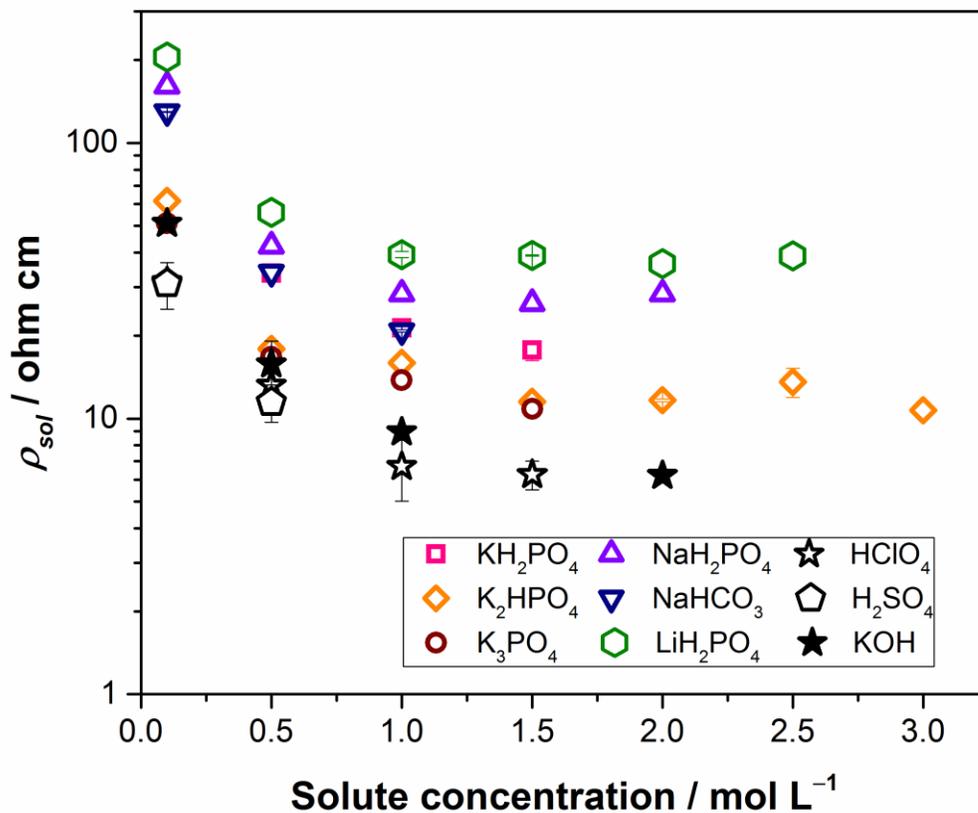


Figure S8. Solution resistivities of the various electrolytes measured by impedance spectroscopy at 298 K (amplitude 10 mV, 100-200 kHz) in a cell with a cell constant of 1.55 cm⁻¹, adopted from our previous study.^[S1]

References

- [S1] T. Shinagawa, K. Takanabe, *J. Phys. Chem. C*, **2016**, *120*, 1785–1794.
- [S2] B. J. Trzeźniewski, O. Diaz-Morales, D. A. Vermaas, A. Longo, W. Bras, M. T. M. Koper, W. A. Smith, *J. Am. Chem. Soc.*, **2015**, *137*, 15112–15121.
- [S3] W. M. Haynes, D. R. Lide, *Handbook of Chemistry and Physics*, 92nd ed.; CRC Press: Boca Raton, FL, **2011**.
- [S4] R. N. Roy, J. J. Gibbons, R. Williams, L. Godwin, G. Baker, J. M. Simonson, K. S. Pitzer, *J. Chem. Thermodynamics*, **1984**, *16*, 303–315.
- [S5] J. K. Kielland, *J. Am. Chem. Soc.*, **1937**, *59*, 1675–1678.
- [S6] T. Shinagawa, K. Takanabe, *ChemSusChem*, **2017**, *10*, 1318–1336.
- [S7] A. K., Covington, K. E. Newman, *J. Inorg. Nucl. Chem.*, **1973**, *35*, 3257–3262.