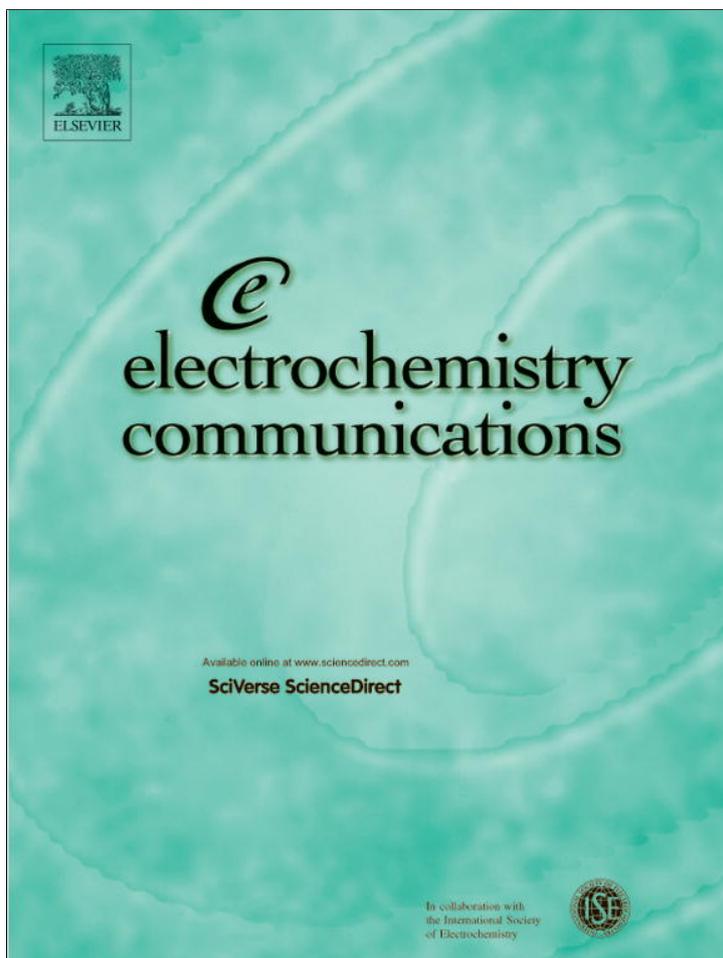


Provided for non-commercial research and education use.
Not for reproduction, distribution or commercial use.



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/authorsrights>



Contents lists available at SciVerse ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

Reliable reference electrodes for lithium-ion batteries

F. La Mantia¹, C.D. Wessells, H.D. Deshazer, Yi Cui*

Department of Materials Science and Engineering, Stanford University, Stanford, CA 94305, USA

ARTICLE INFO

Article history:

Received 2 March 2013

Accepted 11 March 2013

Available online 17 March 2013

Keywords:

Reference electrode

Lithium-ion batteries

Polarizability

High current rate

ABSTRACT

Despite the high attention drawn to the lithium-ion batteries by the scientific and industrial community, most of the electrochemical characterization is carried out using poor reference electrodes or even no reference electrode. In this case, the performances of the active material are inaccurate, especially at high current densities. In this work we show the error committed in neglecting the polarizability of lithium counter electrodes, and we propose two reference electrodes to use in organic electrolytes based on lithium salts, namely $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and LiFePO_4 . In particular, it was observed that, the polarizability of the metallic lithium counter electrode has a relevant stochastic component, which renders measurements at high current densities (above $1 \text{ mA} \cdot \text{cm}^{-2}$) in two electrode cells non reproducible.

© 2013 Published by Elsevier B.V.

1. Introduction

Lithium-ion batteries are very popular due the high energy density and power density they can reach; these are important characteristics for application in the portable electronics market and the automotive market. In particular, the performances of electro-active materials, even at high current rates, are often investigated in two electrodes cell configuration [1,2], although also measurements with reference electrode on whole batteries are reported [3]. In two electrodes setup the total voltage of the cell is measured, and therefore it is not suitable for study of single electrodes. It is usually assumed that metallic lithium electrodes have a negligible overpotential.

Reference electrodes are very important to study the reaction mechanism of single electrodes in batteries, for both standard galvanostatic cycling and electrochemical impedance spectroscopy. In the latter case, also the cell geometry and the electric asymmetry play a very important role above 1 kHz [4,5]. The typical characteristics of a good reference electrode are: non-polarizability; reliability; and reproducibility [6,7]. The non-polarizability is obtained by choosing electrodes with fast kinetics or high surface area [8]. The reliability is given by the constancy of the potential in time, which makes pseudo-reference electrodes inadequate. The reproducibility of the potential of the reference electrode should be in within 1 mV, and it is obtained by using two-phase systems [7,9]. Three-electrode cells for lithium-ion batteries

typically have metallic lithium as both counter and reference electrode, although sometimes it is substituted by lithium alloys [10]. It is noteworthy to stress that the potential of metallic lithium is dependent on the mechanical treatment (native passive film), and is affected by aging. At short time, there is a shift of the potential of metallic lithium with the time due to the formation of the SEI layer and solvated electrons [11]. Thereafter, if the lithium is properly cleaned, the potential of the metallic lithium is stable for several days [12].

In this work we showed the limitations of the metallic lithium and investigated the possibility to use both $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and LiFePO_4 powders as reference electrodes in organic electrolytes containing lithium based salts. Both systems give two-phase reactions upon intercalation or deintercalation with lithium, with a stable and constant equilibrium potential (reproducibility and reliability), able to observe the electrochemical potential of lithium-ion in solution (reliability). Moreover both active materials have reaction potentials located inside the stability window of the EC:DMC and EC:DEC electrolytes, typically used in lithium-ion batteries (reliability).

2. Experimental

Powder of $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ (NMC) and $\text{LiTi}_2(\text{PO}_4)_3$ were synthesized following polymer method and pechini method respectively [13,14], while commercial powder of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (Sud-Chemie) and LiFePO_4 (EEES) were used. A slurry containing 80% active material, 8% PVdF, 3% KS-6 (TIMREX, Timcal), and 9% Super-P (TIMREX, Timcal) in N-methylpyrrolidone (Sigma-Aldrich) was used for $\text{Li}_4\text{Ti}_5\text{O}_{12}$, LiFePO_4 , and $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ electrodes. A slurry containing 78% active material, 9% PVdF, 4% KS-6 (TIMREX, Timcal), and 9% Super-P (TIMREX, Timcal) in N-methylpyrrolidone (Sigma-Aldrich) was used for $\text{LiTi}_2(\text{PO}_4)_3$ electrodes. Electrodes

* Corresponding author. Tel.: +1 650 723 4613.

E-mail address: yicui@stanford.edu (Y. Cui).¹ Present address: Zentrum für Elektrochemie, Ruhr-Universität Bochum, 44780 Bochum, Germany.

based on $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ and $\text{LiTi}_2(\text{PO}_4)_3$ were prepared by doctor blading the slurry on an aluminum foil, with a wet thickness of $250\ \mu\text{m}$ (mass loading circa $4.5\ \text{mg}\ \text{cm}^{-2}$). Electrodes based on $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and LiFePO_4 were prepared by drop casting the slurry on an aluminum mesh (Dexmet, $30\ \mu\text{m}$ thick), and have a total thickness of $50\ \mu\text{m}$. The electrodes were dried for 2 h at $80\ ^\circ\text{C}$ in air. After drying, the electrodes were transferred in glow box, heated up to $150\ ^\circ\text{C}$ for 2 h [15]. The preparation cell for the reference electrode contains two lithium electrodes, between which lies an electrode of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ or LiFePO_4 (see Fig. 1a). The standard cell for the investigation of the active materials contains a NMC or $\text{LiTi}_2(\text{PO}_4)_3$ working electrode, a reference electrode previously prepared, and a lithium counter electrode (see Fig. 1b). VMP-3 multipotentiostat (Bio-Logic) was used for the electrochemical preparation and tests.

3. Results and discussion

3.1. Reference electrode preparation and test

After assembling the preparation cell (Fig. 1a), the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ or LiFePO_4 based electrode was used as positive electrode and the two lithium electrodes were short-circuited and used as negative electrode. The $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was fully reduced, then cycled once, and finally oxidized up to half of its total charge. The LiFePO_4 based electrode was oxidized and reduced and finally oxidized again up to half of its total charge. The applied current rate was $10\ \text{mA}\cdot\text{g}^{-1}$. The resulting potential profiles are reported in Fig. 1c–d. To obtain a reference potential as much reproducible as possible, the electrode was stopped always at half charge during the lithium extraction, so that diffusion

polarization is avoided. After the preparation, the two metallic lithium electrodes were separated and used as working and counter electrode, while the LiFePO_4 or $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode was used as reference; the cell was left at open circuit for 2 h and the potential measured. It was observed that the potential of the two lithium electrodes could differ up to 5 mV.

With the new configuration, the polarizability of lithium could be tested. During this test, a constant current was applied and the potentials of both working (Li1) and counter (Li2) electrodes were measured. The current density was changed every 5 min, starting from $4.44\ \mu\text{A}\cdot\text{cm}^{-2}$ to $4.44\ \text{mA}\cdot\text{cm}^{-2}$ (apparent surface area); before increasing the current density, its value was inverted for other 5 min. When the current density is low, the potential of the metallic lithium stabilizes fast and is reproducible. When the current density is above $1\ \text{mA}\cdot\text{cm}^{-2}$, the potential of the lithium electrodes is not stable in time and is not reproducible, mainly due to the formation of dendrites (Fig. 2a–b). After this galvanostatic treatment the potential of the two metallic lithium electrodes was differing less than 1.5 mV.

The potential of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and LiFePO_4 reference electrodes built in this way in a EC:DMC (1:1) 1 M LiPF_6 electrolyte solution is highly reproducible, and it is equal to 1.567 ± 0.0025 and $3.428 \pm 0.0005\ \text{V}$ vs. Li/Li^+ , respectively (averaged on 10 electrodes). To test the non-polarizability of the reference electrode, and of the impedance spectra of the reference electrode and of the metallic lithium has been measured in the frequency range 100 kHz–0.1 Hz (see Fig. 2c). The measurements were performed in the configuration of Fig. 1a, using once a metallic lithium as working electrode (WE) and the lithium titanate as reference electrode

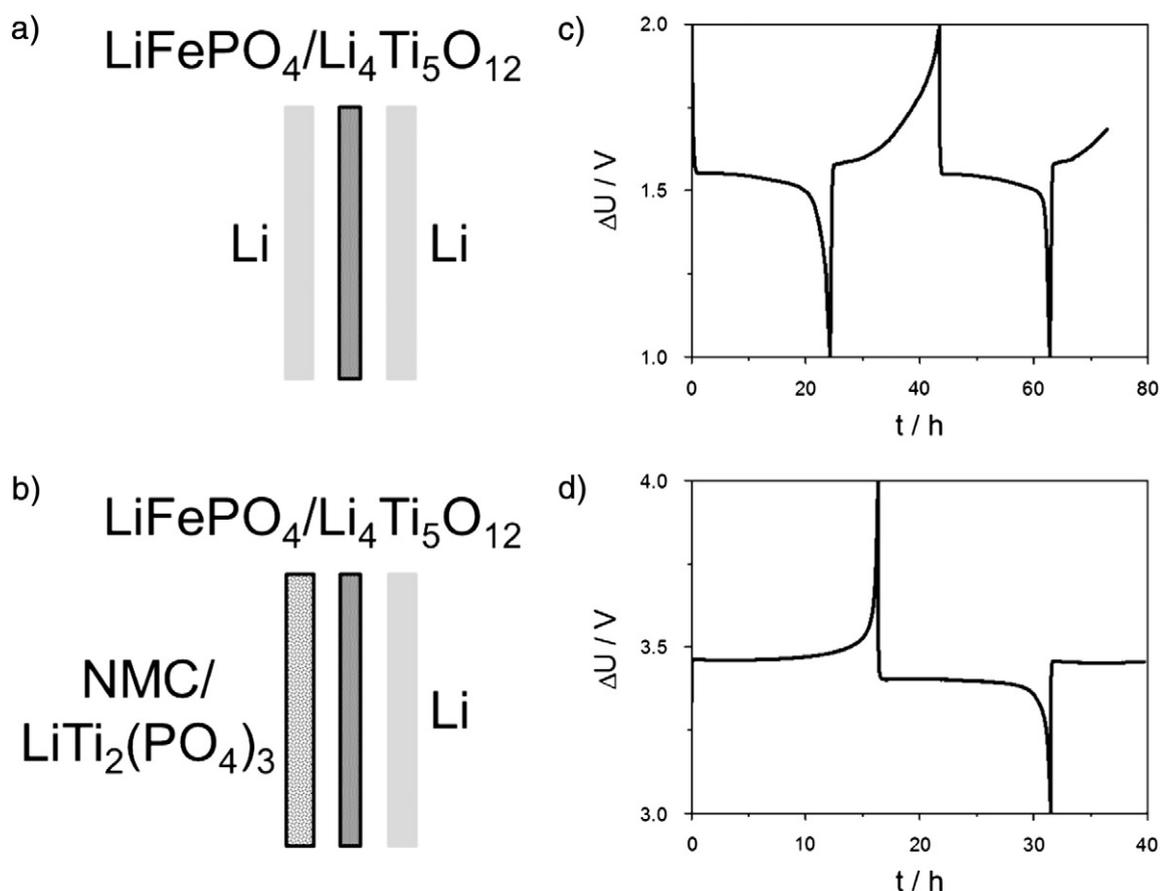


Fig. 1. Schematic picture of the cell arrangement in (a) the preparation cell and (b) the test cell. (c) Charge/discharge profile of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ vs. Li during the reference electrode preparation. (d) Charge/discharge profile of LiFePO_4 vs. Li during the reference electrode preparation.

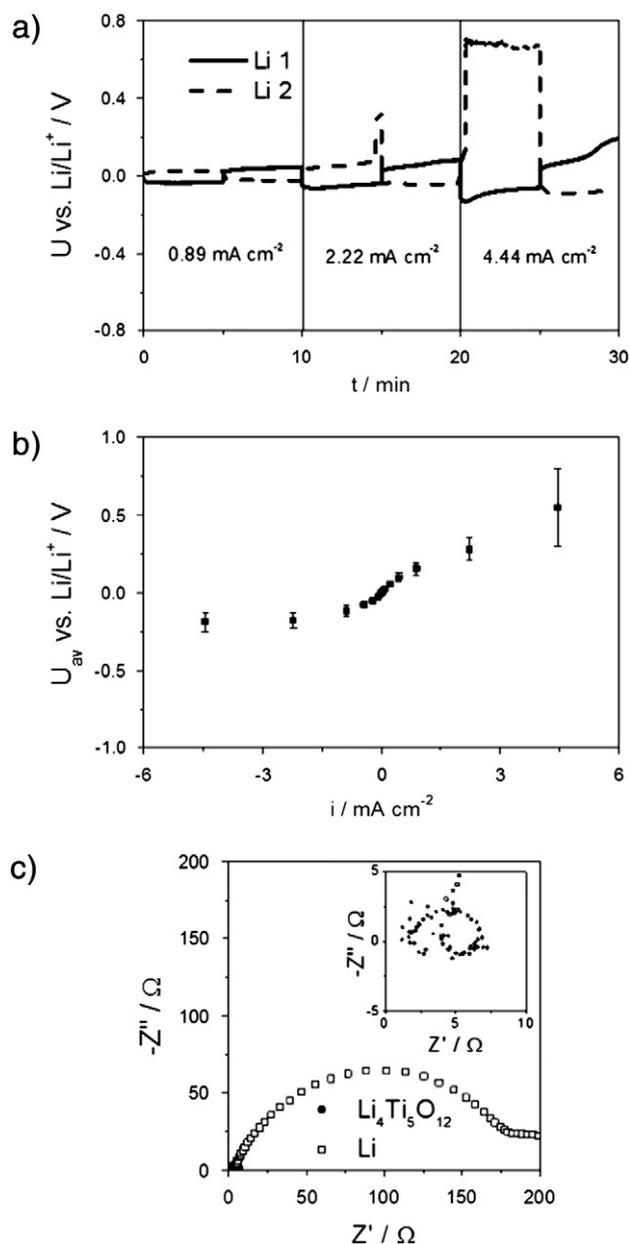


Fig. 2. (a) Polarization experiments on metallic lithium at different current densities. (b) Average polarization potential at different current densities and scattering (error bar). (c) Impedance spectra at open circuit potential of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and metallic lithium.

(RE), and later inverting the two electrodes. It has to be stressed, that the value of the impedance of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is more than one order of magnitude lower than the value of the impedance of metallic lithium. The spectrum of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ looks distorted due to position of the reference electrode and electric asymmetries. While the potential of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ reference electrode tends to drift after some hours of exposure to air, the potential of the LiFePO_4 reference electrode is stable for weeks in air, and can be used in water [14].

3.2. Effect of the reference electrode at high current rates

After the testing, the preparation cell is transferred in glove box and the reference electrode is carefully removed from the cell. The

Table 1

Charge efficiency measured with respect to the working electrode, η_{WE} , whole cell, $\eta_{\text{WE-CE}}$, and relative difference in reversible charge, $\Delta Q/Q_{\text{WE}}$, ΔQ being $Q_{\text{WE}} - Q_{\text{WE-CE}}$.

	$\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$		LiFePO_4	
	20 mA g^{-1}	100 mA g^{-1}	20 mA g^{-1}	100 mA g^{-1}
η_{WE}	0.971	0.999	0.952	0.995
$\eta_{\text{WE-CE}}$	0.969	0.985	0.949	0.966
$\Delta Q/Q_{\text{WE}}$	1.3%	10.7%	0.9%	3.4%

reference electrode can be used in a standard coffee bag three-electrode cell, in the configuration of Fig. 1b. Two different active materials were tested, namely $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ and $\text{LiTi}_2(\text{-PO}_4)_3$, the former a single phase and the latter a two-phase system. All the potentials reported are corrected by the value of the reference electrode and are displayed against Li/Li^+ . In Fig. 3a–b the charge/discharge profiles of a $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ based electrode at 20 mA g^{-1} and 100 mA g^{-1} are shown. The potential limits of 4.3 and 3.0 V vs. Li/Li^+ were set on U_{WE} . For a better comparison, both the potential of the working electrode, U_{WE} , and the total cell voltage, $U_{\text{WE-CE}}$, are reported. The charge efficiency and reversible specific charge can be calculated for the potential limit applied to U_{WE} (η_{WE} and Q_{WE}) or to $U_{\text{WE-CE}}$ ($\eta_{\text{WE-CE}}$ and $Q_{\text{WE-CE}}$). At higher current rates and current densities the effect of the reference electrode becomes significant, showing a noticeable difference between η_{WE} and $\eta_{\text{WE-CE}}$ (from almost 1 to 0.985) as well as between Q_{WE} and $Q_{\text{WE-CE}}$ (10.7% less) (see Table 1). In Fig. 3c–d the charge/discharge profiles of a $\text{LiTi}_2(\text{PO}_4)_3$ based electrode at 20 mA g^{-1} and 100 mA g^{-1} are reported. Also in this case, the potential limits of 3.0 and 2.0 V vs. Li/Li^+ were set on U_{WE} . In the two-phase system the difference between Q_{WE} and $Q_{\text{WE-CE}}$ is smaller and equal to 3.4%. Although the current rates and current densities are very similar, the two different materials were tested with two different pieces of lithium, and it is immediately evident that the difference between the total voltage and the electrode potential is not the same for Fig. 3b–d. This phenomenon is due to the stochastic behavior of the lithium counter electrode at high current densities. On the opposite, at low rates (Fig. 3a–c), the lithium has reproducible potential. By increasing the current rate, the reversible specific charge decreases and the difference between the potential of the working electrode and the voltage of the full cell increases and becomes time-dependent.

4. Conclusions

We have shown that a highly reproducible reference electrode for lithium-ion batteries can be built, starting from $\text{Li}_4\text{Ti}_5\text{O}_{12}$ or LiFePO_4 . After preparation, the two reference electrodes show a potential of 1.567 ± 0.0025 and 3.428 ± 0.0005 V vs. Li/Li^+ , respectively. The reference electrodes show low polarizability. The importance of the reference electrode in the high current rates has been demonstrated by using two systems, namely $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ and $\text{LiTi}_2(\text{PO}_4)_3$. In the former case, the reference electrode plays a major role, because of the incomplete deintercalation of lithium from the active material. The behavior of lithium becomes stochastic at current densities above $1 \text{ mA}\cdot\text{cm}^{-2}$, due to the dendrite formation.

Acknowledgments

Work supported by the Global Climate and Energy Project at Stanford and King Abdullah University of Science and Technology (KAUST) under the award no. KUS-I1-001-12.

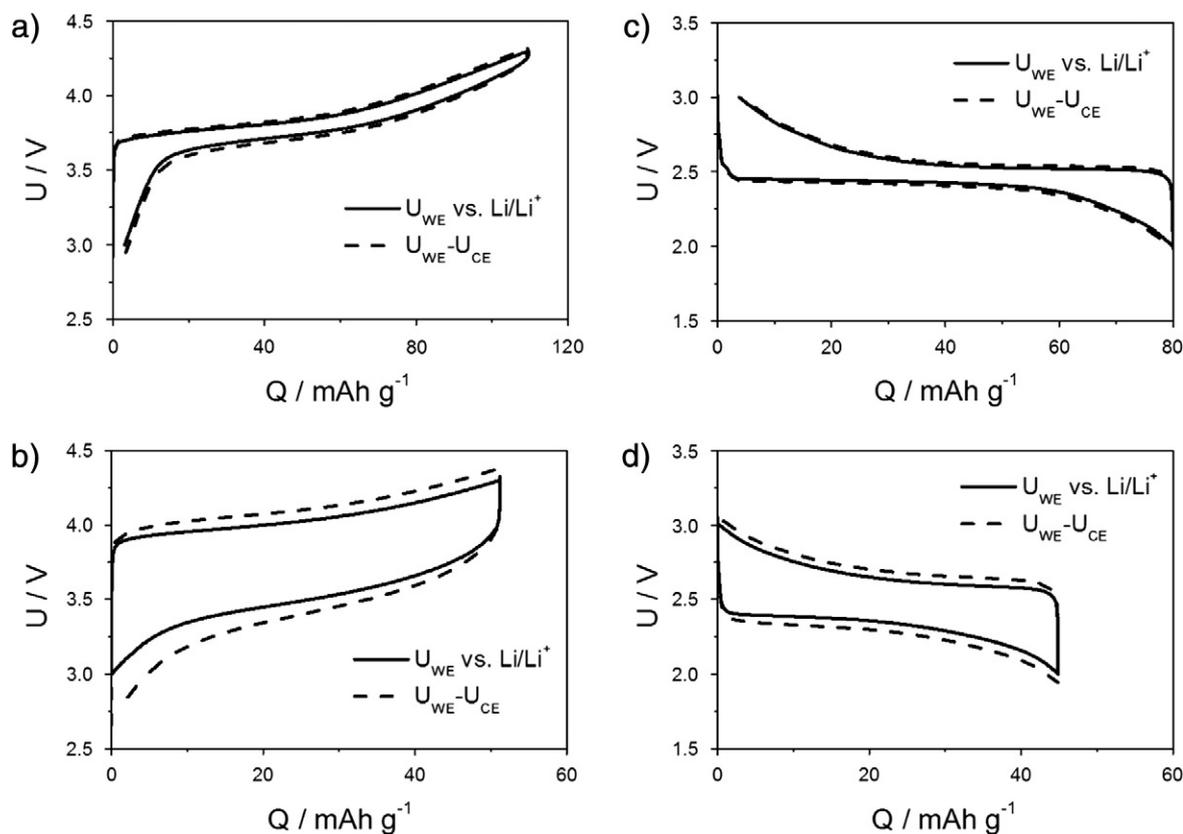


Fig. 3. Potential profile of charge and discharge of $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ at (a) 20 mA g^{-1} and (b) 100 mA g^{-1} . Potential profile of charge and discharge of $\text{LiTi}_2(\text{PO}_4)_3$ at (c) 20 mA g^{-1} and (d) 100 mA g^{-1} . Both potential of the working electrode (U_{WE}) and total voltage of the cell ($U_{WE}-U_{CE}$) are reported.

References

- [1] H. Buqa, D. Goers, M. Holzapfel, M.E. Spahr, P. Novák, *Journal of the Electrochemical Society* 152 (2005) A474.
- [2] S.W. Lee, N. Yabuuchi, B.M. Gallant, S. Chen, B.S. Kim, P.T. Hammond, Y. Shao-Horn, *Nature Nanotechnology* 5 (2010) 531.
- [3] Q.W. Wu, W.Q. Lu, J. Prakash, *Journal of Power Sources* 88 (2000) 237.
- [4] M. Ender, A. Weber, E. Ivers-Tiffée, *Journal of the Electrochemical Society* 159 (2012) A128.
- [5] S. Klink, E. Madej, E. Ventosa, A. Lindner, W. Schuhmann, F. La Mantia, *Electrochemistry Communications* 22 (2012) 120.
- [6] A. Blyr, C. Sigala, G. Amatucci, D. Guyomard, Y. Chabre, J.M. Tarascon, *Journal of the Electrochemical Society* 145 (1998) 194.
- [7] M. Dolle, F. Orsini, A.S. Gozdz, J.M. Tarascon, *Journal of the Electrochemical Society* 148 (2001) A851.
- [8] F. Mansfeld, S. Lin, Y.C. Chen, H. Shih, *Journal of the Electrochemical Society* 135 (1988) 906.
- [9] M. Pasta, A. Battistel, F. La Mantia, *Electrochemistry Communications* 20 (2012) 145.
- [10] D.P. Abraham, S.D. Poppen, A.N. Jansen, J. Liu, D.W. Dees, *Electrochimica Acta* 49 (2004) 4763.
- [11] D. Rahner, *Journal of Power Sources* 81–82 (1999) 358.
- [12] B. Burrows, R. Jasinski, *Journal of the Electrochemical Society* 115 (1968) 365.
- [13] H.D. Deshazer, F. La Mantia, C. Wessells, R.A. Huggins, Y. Cui, *Journal of the Electrochemical Society* 158 (2011) A1079.
- [14] C.D. Wessells, F. La Mantia, H.D. Deshazer, R.A. Huggins, Y. Cui, *Journal of the Electrochemical Society* 158 (2011) A352.
- [15] F. La Mantia, R.A. Huggins, Y. Cui, *Journal of Applied Electrochemistry* 43 (2013) 1.