Towards Implantable Bio-Supercapacitors: Pseudocapacitance of Ruthenium Oxide Nanoparticles and Nanosheets in Acids, Buffered Solutions, and Bioelectrolytes

Sho Makino, Takayuki Ban, and Wataru Sugimoto

1Materials and Chemical Engineering, Faculty of Textile Science and Technology, Shinshu University, Ueda, Nagano 386–8567, Japan
2Center for Energy and Environmental Science, Interdisciplinary Cluster for Cutting Edge Research, Shinshu University, Ueda, Nagano 386–8567, Japan

Metal oxides, in particular ruthenium-based oxides, are promising electrode materials for aqueous pseudocapacitors. Strong acids or bases are favored over neutral electrolytes owing to the higher capacitance. Here we explore the pseudocapacitive behavior of ruthenium oxide nanoparticles and nanosheets in near neutral pH as an environmentally benign electrolyte. The pseudocapacitive charge storage in poorly-crystalline hydrous RuO2 nanoparticles, and highly-crystalline RuO2 nanosheets were investigated in acetic acid-lithium acetate (AcOH-AcOLi) buffered solutions. It is shown that capacitance values as high as 1.038 F g⁻¹ can be achieved in AcOH-AcOLi buffered solutions with RuO2 nanosheets, which is 44% higher than the benchmark RuO2·nH2O in H2SO4 electrolyte (720 F g⁻¹). Furthermore, comparable performance was obtained in phosphate buffered saline and fetal bovine serum. The mechanism of the pseudocapacitive properties is discussed based on the difference in the surface redox behavior of different RuO2 nanoparticles and nanosheets in near neutral pH,20 suggesting the possibility of other new electrolytes.

In this study, emphasis was placed on elucidating the origin and mechanism of the pseudocapacitive of ruthenium based oxides in buffered solutions. Three different nanostructured RuO2 materials were studied; namely poorly crystalline hydrous RuO2 nanoparticles, well-crystalline anhydrous RuO2 nanoparticles, and crystalline RuO2 nanosheets. The capacitive behavior of these materials were studied in H2SO4 as the acidic electrolyte, or Li2SO4 or AcOLi as neutral electrolyte. Various AcOH-AcOLi buffer solutions with different ionic strength (constant pH) were used, and the ratio of weak acid/conjugated base ratio was also varied. In addition, the role of weak acid was investigated by adding a small amount of AcOH to a supporting electrolyte (Li2SO4). Furthermore, phosphate buffered saline and fetal bovine serum were studied as bioelectrolytes for application toward implantable bio-supercapacitors.

Experimental

Ultrapure water (Milli-Q, > 18 MΩ cm) was used for all synthesis and characterization. RuO2·nH2O was prepared by a modified sol-gel process following literature.18,19 In a typical synthesis, a 0.3 M NaOH solution was slowly added to a 0.1 M aqueous RuCl3 solution while maintaining a constant pH value of 7. The precipitate was collected and washed thoroughly to remove by-products. The product was suspended in H2O and aged for 72 h at 40°C. The powder samples were collected and heat treated in air at 150°C for 17 h to obtain RuO2·nH2O (n = 0.5). Anhydrous RuO2 was prepared by calcination of RuO2·nH2O (Johnson Matthey) at 450°C for 2 h.

Ruthenium oxide nanosheets (RuO2ns) were synthesized following a previously reported method.23 Briefly, α-NaFeO2 type NaRuO2 was synthesized by solid state reaction of Na2CO3, Ru and Ru2O3 (2:1:3 molar ratio) at 900°C for 12 h under Ar atmosphere. Oxidative

Electrochemical capacitors (also known as supercapacitors) are energy harvesting devices capable of charge and discharging within a few seconds, and cycle life in the order of thousands of cycles. Some metal-oxides are known to provide high capacitance in aqueous electrolytes, owing to the combination of the non-faradaic electrical double layer charging and the faradic surface or near surface confined redox capacitance (pseudocapacitance).1 Pseudocapacitance is a phenomenon generally observed in aqueous electrolytes.2 Acidic or basic electrolytes such as H2SO4 and KOH are favorable in terms of power density owing to the high conductivity. RuO2 is one of the rare oxides that is stable in both acidic and basic conditions. Hydrous RuO2 nanoparticles (RuO2·nH2O; where n is typically 0.5) offers capacitance of ~700 F g⁻¹ in H2SO4 electrolyte and can be cycled for thousands of cycles with practically no decay, thus is often used for performance benchmarking of new electrode materials. Although studies on the asymmetric systems and applicability of non-aqueous electrolytes to oxide electrodes in order to widen the operating voltage window have recently been initiated, non-aqueous electrolytes have yet to surpass aqueous electrolytes in terms of specific capacitance.3,4

Electrolytes near neutral pH are selected for materials that are not as corrosion-resistant in acids and base, for example manganese oxide.9,10 Neutral electrolytes are more environmentally benign and its low corrosiveness allows a wider range in choice for periphery material, such as current collectors and packaging.13 Despite the RuO2-based material being the model pseudocapacitive material, studies on the electrochemical capacitor behavior in neutral electrolytes are scarce compared to the more popular acidic or basic electrolytes. One of the reasons is that the capacitance of RuO2 in neutral electrolytes is generally 1/2 of that in sulfuric acid or potassium hydroxide.14-17 Nonetheless, the use of neutral pH electrolytes has advantages when used for asymmetric (hybrid) supercapacitors, which are devices that utilize different materials (e.g. metal oxides, carbon, etc) for the positive and negative electrodes.32 In such a case, the operating voltage window can be extended beyond the thermodynamic 1.2 V limit if the kinetics of gas evolution is extremely slow. Up to now, alkali metal sulfates, nitrates, and chlorides have been used as neutral electrolytes.

We have also used Li2SO4 as the electrolyte for our hybrid supercapacitors based on protected Li anode technology.18-20 This hybrid supercapacitor utilizes a Li ion conducting glass ceramic membrane, which is stable within a limited pH range. We recently communicated that unprecedented capacitance values exceeding that of H2SO4 can be achieved by using an acetic acid-lithium acetate (AcOH-AcOLi) buffered solution with near neutral pH,20 suggesting the possibility of other new electrolytes.

Received December 2, 2014; revised manuscript received December 26, 2014. Published January 9, 2015. This paper is part of the JES Focus Issue on Electrochemical Capacitors: Fundamentals to Applications.

*E-mail: wsugi@shinshu-u.ac.jp

© The Author(s) 2015. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.002150jes] All rights reserved.
de-intercalation of Na\(^+\) with aqueous Na\(_2\)S\(_2\)O\(_8\) and subsequent proton exchange in 1 M HCl leads to the layered H\(_0.2\)RuO\(_2\) \(\cdot\) 0.5H\(_2\)O. The layered ruthenic acid was added to a tetrabutylammonium hydroxide (TBAOH) aqueous solution with the molar ratio of TBA ions to \(n\)H\(_2\)O adjusted to TBA\(^+/\)H\(^+\) \(=\) 5. The dispersion was vigorously shaken for 10 days to exfoliate the layered ruthenate into elementary RuO\(_2\) nanosheets. The resultant suspension was centrifugated at 2,000 rpm for 30 min to remove trace amounts of impurity Ru metal and non-exfoliated material.

Electrochemical measurements were carried out using a beaker-type electrochemical cell composed of a Pt mesh counter electrode and a Ag/AgCl/KCl (sat.) reference electrode connected with a salt bridge. A Luggin capillary faced the working electrode at a distance of \(\sim\)2 mm. Electrode potentials will be referred to the reversible hydrogen electrode (RHE). A broad redox process above 0.8 V and below 0.6 V vs RHE on the anodic and cathode scans, respectively. The rectangular background current is superimposed for the other electrolytes and a slow irreversible redox process above 0.8 V and below 0.6 V vs RHE on the anodic and cathode scans, respectively.

The cyclic voltammograms in 1.0 M Li\(_2\)SO\(_4\) are characterized by a rectangular background current (shown as shaded region in the figure), and a slow irreversible redox process above 0.8 V and below 0.6 V vs RHE on the anodic and cathode scans, respectively. The rectangular background current is superimposed for the other electrolytes and a slow irreversible redox process above 0.8 V and below 0.6 V vs RHE on the anodic and cathode scans, respectively.

The behavior in 2.0 M AcOH is similar to Li\(_2\)SO\(_4\) in many aspects. The capacitance values in AcOH and Li\(_2\)SO\(_4\) are both \(~200\) F g\(^{-1}\) from the scan rate independent region. This capacitance translates to an estimated surface area of 1,000 m\(^2\) g\(^{-1}\) or 1.0 nm particle size, taking the value of 20 \(\mu\)F cm\(^{-2}\) as a probe value for area specific capacitance. This particle size is in good agreement with the local structure derived by EXFAS\(^2\) and SAXS.\(^3\)

The pseudocapacitance due to surface redox processes \(C_{\text{redox}}\) is calculated by subtracting \(C_{\text{dl}}\) from the overall capacitance \(C\) at the respective scan rates and is shown in Fig. 1B. The slow irreversible redox process above 0.8 V and below 0.6 V can be interpreted as the dissociative adsorption of water according to reaction 1.\(^{1,16}\)

\[
\text{Ru}_2\text{O}_3 + \text{H}_2\text{O} = 2\text{RuO}_2 + 2\Theta + 2\text{H}^+ \quad [1]
\]

The behavior in 2.0 M AcOH is similar to Li\(_2\)SO\(_4\) in many aspects. The \(C_{\text{dl}}\) values in AcOH and Li\(_2\)SO\(_4\) are both \(~200\) F g\(^{-1}\). The redox peaks due to reaction 1 is observed at \(E_{1/2} = 0.70\) V, which is close to

### Table I. List of buffered solutions used.

| Electrolyte                        | Mixing volume ratio | pH   | Conductivity/ S m\(^{-1}\) |
|------------------------------------|---------------------|------|----------------------------|
| 0.5 M AcOH - AcOLi                 | 12.5 : 87.5         | 5.4  | 2.15                       |
| 2.0 M AcOH - AcOLi                 | 12.5 : 87.5         | 5.4  | 3.35                       |
| 2.0 M AcOH - AcOLi                 | 58.5 : 41.5         | 4.4  | 3.04                       |
| 2.0 M AcOH - AcOLi                 | 95.0 : 5.0          | 3.3  | 0.586                      |
| 5.0 M AcOH - AcOLi                 | 12.5 : 87.5         | 5.4  | 3.76                       |
| 0.1 M AcOH + 1.0 M Li\(_2\)SO\(_4\) | 5.0 : 95.0          | 4.2  | 6.87                       |
| Phosphate buffered saline          | –                   | 7.3  | –                          |
| Fetal bovine serum                 | –                   | 7.4  | –                          |

---

**Figure 1.** (A) Cyclic voltammograms of RuO\(_2\) \(\cdot\) nH\(_2\)O in a) 0.5 M H\(_2\)SO\(_4\), b) 1.0 M Li\(_2\)SO\(_4\), c) 2.0 M AcOLi, and d) 2.0 M AcOH-AcOLi at 60°C with \(v\) = 2, 5, 20, 50, 200, and 500 mV s\(^{-1}\). (B) The overall capacitance deconvoluted into the electrical double layer capacitance \(C_{\text{dl}} = 200\) F g\(^{-1}\) and redox capacitance \(C_{\text{redox}}\).
to the Ru$^{4+}$/Ru$^{3+}$ potential according to the Pourbaix diagram$^{26}$ for this reaction. An obvious difference is the charge related to reaction 1; the charge is higher in 2.0 M AcOLi. This difference may be due to specific adsorption of SO$_2^{2-}$ on the oxide surface, hindering the adsorption of water, and thus delaying reaction 1.

The behavior in 2.0 M AcOH-AcOLi seems to be a combination of the behavior in H$_2$SO$_4$ and AcOLi depending on the scan rate. At slow scan rates the voltammograms are similar to that in H$_2$SO$_4$ and a capacitance of 687 F g$^{-1}$ at 2 mV s$^{-1}$ is obtained. On the other hand, only electrical double layer charging occurs at fast scan rates in AcOLi, reducing the capacitance to 210 F g$^{-1}$ at 500 mV s$^{-1}$. This phenomenon (lack of pseudocapacitance at high scan rates) is due to the low proton concentration in 2.0 M AcOH-AcOLi. Surface redox phenomenon (lack of pseudocapacitance at high scan rates) is due to the adsorption of AcOH (discussed in detail later).

The charge is higher in 2.0 M AcOLi. This difference may be due to reaction 1. An obvious difference is the charge related to reaction 1; the capacitive effect in H$_2$SO$_4$, which originates from the above mentioned treatment. The charge is, however, only electrical double layer charging in AcOLi, reducing the capacitance to 210 F g$^{-1}$ at 500 mV s$^{-1}$.

The pseudocapacitive behavior of anhydrous RuO$_2$ nanoparticles in 0.5 M H$_2$SO$_4$, 1.0 M Li$_2$SO$_4$, 2.0 M AcOLi, and 2.0 M AcOH-AcOLi are qualitatively similar to RuO$_2$·nH$_2$O (Fig. S1). The change in molarity of AcOH-AcOLi between 0.5 and 5.0 M does not affect the voltammograms significantly (Fig. S2). At the lowest concentration of 0.5 M, a peak at $E_{1/2} = 0.41$ V evolves at slow scan rate, which is attributable to the adsorption of AcOH (discussed in detail later).

**Pseudocapacitive properties of RuO$_2$ nanosheets in various electrolytes.**—Cyclic voltammograms of RuO$_2$ nanosheets in 0.5 M H$_2$SO$_4$, 1.0 M Li$_2$SO$_4$, 2.0 M AcOLi, and 2.0 M AcOH-AcOLi are shown in Fig. 2A. The voltammograms in 0.5 M H$_2$SO$_4$ are quite different from sol-gel derived RuO$_2$·nH$_2$O nanoparticles in that there is a distinctive large redox pair at $E_{1/2} = 0.64$ V vs. RHE. The capacitance at 2 mV s$^{-1}$ is 831 F g$^{-1}$ and decreases by 15% to 703 F g$^{-1}$ at 500 mV s$^{-1}$. Following the case for RuO$_2$·nH$_2$O nanoparticles, the C$_d$ value can be deduced from the constant $dq$ at E$=-0.6$ V. The capacitive effect in H$_2$SO$_4$ and AcOH-AcOLi represents 50 to 70% of the overall capacitance.

The distinctive redox peaks observed for RuO$_2$ nanosheets changes drastically when the ionic strength of the AcOH-AcOLi buffer solution is changed while keeping a constant pH (Fig. S3). The redox pair at $E_{1/2} = 0.41$ V is strongly dependent on the ionic strength, broadening and decreasing in charge with decreasing AcOH-AcOLi concentration. The $E_{1/2} = 0.60$ V peak is less dependent on the AcOH-AcOLi concentration. These observations can be attributed to decreasing concentration of the active species. It is noted that at the highest concentration of 5.0 M AcOH-AcOLi, a remarkable capacitance of 1,038 F g$^{-1}$ is obtained.$^{20}$

**Figure 2.** (A) Cyclic voltammograms of RuO$_2$ nanosheets in a) 0.5 M H$_2$SO$_4$, b) 1.0 M Li$_2$SO$_4$, c) 2.0 M AcOLi, and d) 2.0 M AcOH-AcOLi at 60°C with $v = 2$, 5, 20, 50, 200, and 500 mV s$^{-1}$. (B) The overall capacitance deconvoluted into the electrical double layer capacitance (C$_d$ = 300 F g$^{-1}$) and redox capacitance (C$_{redox}$).
In order to gain further insight into the origin of the redox peaks, the pH of the buffer solution was controlled by changing the salt/supporting electrolyte volumetric ratio. As shown in Fig. 3, as the pH is lowered, the cyclic voltammograms become strongly scan rate dependent, which is due to the decrease in the conductivity of the buffer solutions. Figure 3d compares the voltammograms at 2 mV s$^{-1}$. The $E_{1/2} = 0.60$ V vs RHE peak is independent of pH (note that in H$_2$SO$_4$, the $E_{1/2} = 0.41$ and 0.60 V vs RHE peaks overlap). The $E_{1/2} = 0.60$ V vs RHE peak is attributed to reaction 1, similar to the case for RuO$_2$ $\cdot$ nH$_2$O nanoparticles. The $E_{1/2} = 0.41$ V vs RHE (at pH = 5.43) shifts to positive potentials as the pH is decreased. This peak shows a linear relation with pH (Fig. 4), suggesting that it is related to adsorption of protons or hydrated protons. Analysis of the slope shows that this is a 1.5 electron reaction, or 3 electrons per 2 reaction sites. This irregular behavior is consistent with previous studies on hydrous metal oxide films of Ir and Ru$^{29-31}$.

Figure 5 shows comparative data of the change in pH for RuO$_2$ $\cdot$ nH$_2$O nanoparticles. The cyclic voltammograms for H$_2$SO$_4$ and 2.0 M AcOH-AcOLi (pH = 5.36) completely overlap, suggesting an analogous charge storage mechanism. On the other hand, the electrochemical behavior in 2.0 M AcOH-AcOLi with pH = 4.44 and 3.42 are quite different. For pH = 3.42, the electrical double layer capacitance is completely lost. We attribute this peculiarity to adsorption of molecular AcOH (not AcO$^-$) on the surface of RuO$_2$, blocking the electrical double layer formation. As the pH is lowered, the relative content of AcOH increases (Table I). In the case of 2.0 M AcOH-AcOLi (pH = 5.36), the adsorption of AcOH is not evident since the concentration of AcOH is much smaller than at pH = 4.44 and 3.42. A similar phenomena was observed for adsorption of CH$_3$OH in H$_2$SO$_4$, where CH$_3$OH is adsorbed on RuO$_2$ $\cdot$ nH$_2$O nanoparticles$^{23}$.

The reason for the absence of AcOH adsorption on RuO$_2$ nanosheets cannot be identified at this point, but it should be noted that CH$_3$OH also does not adsorb on RuO$_2$ nanosheets$^{23}$.

A weak acid in a supporting electrolyte.— Figure 6 shows cyclic voltammograms when a small amount of AcOH was added to Li$_2$SO$_4$ (0.1 M AcOH + 1.0 M Li$_2$SO$_4$, pH = 4.16). At slow scan rates

![Figure 3](image3.png)  
**Figure 3.** Cyclic voltammograms of RuO$_2$ nanosheets at 2, 5, 20, 50, 200, 500 mV s$^{-1}$ in 2.0 M AcOH-AcOLi at pH of a) 3.33, b) 4.49, and c) 5.43. d) Cyclic voltammograms of RuO$_2$ nanosheet at 2 mV s$^{-1}$ in 2.0 M AcOH-AcOLi with various pH and 0.5 M H$_2$SO$_4$.

![Figure 4](image4.png)  
**Figure 4.** Plots of $E_{1/2}$ of redox peaks for RuO$_2$ nanosheets in 2.0 M AcOH-AcOLi and 0.5 M H$_2$SO$_4$ as a function of the pH.
Figure 5. Cyclic voltammograms of RuO$_2$·$n$H$_2$O at 2, 5, 20, 50, 200, 500 mV s$^{-1}$ in 2.0 M AcOH-AcOLi at pH of a) 3.42, b) 4.44, and c) 5.36. d) Cyclic voltammograms of RuO$_2$ nanosheets at 2 mV s$^{-1}$ in 2.0 M AcOH-AcOLi with various pH and 0.5 M H$_2$SO$_4$.

Figure 6. (A) Cyclic voltammograms and (B) deconvoluted of specific capacitance for a) RuO$_2$ nanosheets and b) RuO$_2$·$n$H$_2$O in 0.1 M AcOH-1.0 M Li$_2$SO$_4$ (pH 4.16).
the cyclic voltammograms for RuO2·H2O nanoparticles and RuO2 nanosheets both resemble the behavior in AcOH-AcOli buffered solutions. The capacitance at 2 mV s⁻¹ is 639 and 962 F g⁻¹ for RuO2·H2O nanoparticles and RuO2 nanosheets, respectively. On the other hand, at fast scan rate, the voltammograms are similar to those in Li2SO4, since the concentration of AcOH is very small. This clearly shows that protons contribute to the pseudocapacitive behavior of RuO2-based nanostructures. Thus, an electrolyte composed of a weak acid and a supporting electrolyte can also be used as an electrolyte for pseudocapacitors. Buffered solutions have the advantage of pH control, ionic strength, and biocompatibility, compared to a weak acid in supporting electrolyte. However, the finding that such a simple mixture can be used as an electrolyte for pseudocapacitors paves the way to a massive combination of new electrolytes to explore.

Bio-supercapacitor based on phosphate buffered saline and fetal bovine serum.— Besides the benefit of control in pH and ionic strength, buffered solutions have the advantage of biocompatibility, as many buffers exist in nature (sea water, blood, internal cell fluids, cells and tissues). Here we demonstrate the use of phosphate buffered saline and fetal bovine serum as bioelectrolytes for supercapacitors applicable to safe and bio-compatible implantable power sources. Figure 7 shows the cyclic voltammograms of RuO2 nanosheets in phosphate buffered saline and fetal bovine serum at 25°C. The redox behavior and capacitance are similar to the AcOH-AcOli system. The specific capacitance at 2 mV s⁻¹ in phosphate buffered saline was 837 F g⁻¹, and 772 F g⁻¹ in fetal bovine serum. These values are at least twice as large as those of MWCNTs/PANI composite in physiological electrolyte and human serum. The results potentially show that the combination of pseudocapacitive oxide electrodes and bioelectrolytes can afford exceptionally high energy density.

Conclusions

The electrochemical charge storage in buffered solutions using poorly-crystalline hydrous RuO2 nanoparticles and well-crystalline RuO2 nanosheets as electrode materials was studied. Capacitance comparable to or higher than H2SO4 were obtained in acetic acid-lithium acetate (AcOH-AcOli) buffered solutions, depending on the ionic strength and pH. At constant pH, AcOH-AcOli with higher ionic strength (molarity) lead to higher capacitance, owing to the presence of higher concentration of the adsorbant in the electrolyte. When the pH is varied by changing the volume ratio of AcOH-AcOli, the pseudocapacitive behavior deteriorated with decreasing pH. This phenomenon is discussed based on the decrease in the conductivity of the electrolyte. The highest capacitance of 1.038 F g⁻¹ was obtained in a 5 M AcOH-AcOli (pH = 5.4) with RuO2 nanosheet electrodes. RuO2 nanosheets afforded 20 to 50% higher capacitance than RuO2·H2O in all of the electrolytes studied (H2SO4, Li2SO4, AcOli, AcOH-AcOli, AcOH-Li2SO4). The lower capacitance of RuO2·H2O in AcOH-AcOli is due to the adsorption of AcOH molecules, which hinders the formation of the electrical double layer. Moreover, outstanding performance was obtained in phosphate buffered saline (837 F g⁻¹) and fetal bovine serum (772 F g⁻¹) with RuO2 nanosheet electrodes. The results presented here demonstrate the effective use of bioelectrolytes for pseudocapacitors applicable to environmentally benign, safe and bio-compatible implantable power sources.

Acknowledgments

This work was supported in part by the Advanced Low Carbon Technology Research and Development Program (ALCA) of the Japan Science and Technology Agency (JST) and Chubu Electric Power Co., Inc. W.S. wishes to thank Profs. Akira Teramoto and Koji Abe of Shinshu University for fruitful discussion on the bioelectrolytes. This manuscript is dedicated to the memory of Professor Koji Abe, an excellent researcher and a humble and modest colleague, who passed away suddenly on 18 November, 2014, during the course of the preparation of this manuscript.

References

1. B. Conway, Electrochemical supercapacitors: scientific fundamentals and technological applications, Kluwer Academic/Plenum Publishers, New York, USA, (1999).
2. V. Augustyn, P. Simon, and B. Dunn, Energy Environ. Sci., 7, 1597 (2014).
3. Y. Augustyn, J. Come, M. a Lowe, J. W. Kim, P. L. Taberna, S. H. Tolbert, H. D. Abrutin, P. Simon, and B. Dunn, Nat. Mater., 12, 518 (2013).
4. M. Egashira, T. Uno, N. Yoshimoto, and M. Morita, Electrochemistry, 75, 595 (2007).
5. S. Makino, Y. Takasu, and W. Sugimoto, Chem. Lett., 39, 544 (2010).
6. L. Mayrand-Provencher, S. Lin, D. Lazzerini, and D. Rochefort, J. Power Sources, 195, 5114 (2010).
7. D. Rochefort and A.-L. Pont, Electrochem. Commun., 8, 1539 (2006).
8. K.-H. Chang, C.-C. Hu, C.-M. Huang, Y.-L. Liu, and C.-L. Chang, J. Power Sources, 196, 2387 (2011).
9. H. Y. Lee and J. B. Goodenough, J. Solid State Chem., 148, 81 (1999).
10. H. Y. Lee, V. Manivannan, and J. B. Goodenough, Comptes Rendus Académie des Sci. - Ser. II-Chim., 2, 565 (1999).
11. H. Y. Lee and J. B. Goodenough, J. Solid State Chem., 144, 220 (1999).
12. J. W. Long, D. Bélanger, T. Brousse, W. Sugimoto, M. B. Sassin, and O. Crosnier, MRS Bull., 36, 513 (2011).
13. Z. Chang, Y. Yang, M. Li, X. Wang, and Y. Wu, J. Mater. Chem. A, 2, 10739 (2014).
14. S. Wen, J. Lee, I. Yeo, J. Park, and S. Mho, Electrochim. Acta, 50, 849 (2004).
15. S. Sopić, Z. Mandić, G. Inzelt, M. K. Roković, and E. Meštrović, J. Power Sources, 196, 4849 (2011).
16. S. Sopić, M. K. Roković, Z. Mandić, A. Roka, and G. Inzelt, Electrochim. Acta, 56, 3543 (2011).
17. M. Tomkiewicz, S. Y. Huang, F. H. Poljak, and J. E. Soc, J. Electrochem. Soc., 130, 1514 (1983).
18. W. Shimizu, S. Makino, K. Takahashi, N. Imanishi, and W. Sugimoto, J. Power Sources, 241, 572 (2013).
19. S. Makino, Y. Shimohara, T. Ban, W. Shimizu, K. Takahashi, N. Imanishi, and W. Sugimoto, RSC Adv., 2, 12144 (2012).
20. S. Makino, T. Ban, and W. Sugimoto, Electrochim. Acta, 81, 795 (2013).
21. J. P. Zheng and T. R. Jow, J. Electrochem. Soc., 142, L6 (1995).
22. J. P. Zheng, P. J. Cygan, and T. R. Jow, J. Electrochem. Soc., 142, 2699 (1995).
23. K. Fukuda, T. Saida, J. Sato, M. Yonezawa, Y. Takasu, and W. Sugimoto, Inorg. Chem., 49, 4391 (2010).
24. D. A. McKeown, P. L. Hagnas, L. P. L. Catterall, A. E. Russell, K. E. Swider, and D. R. Rolison, J. Phys. Chem. B, 103, 4825 (2009).
25. N. Yoshida, Y. Yamada, S. Nishimura, Y. Oba, M. Ohnuma, and A. Yamada, J. Phys. Chem. B, 117, 12003 (2013).
26. M. Pourbaix, Atlas of Electrochemical Equilibria in Aqueous Solutions, 2nd ed., National Association of Corrosion Engineers, Houston, Tex., (1974).
27. W. Sugimoto, K. Yokoshima, Y. Murakami, and Y. Takasu, Electrochim. Acta, 52, 1742 (2006).
28. W. Sugimoto, T. Kizaki, K. Yokoshima, Y. Murakami, and Y. Takasu, Electrochim. Acta, 49, 313 (2004).
29. L. D. Burke and O. J. Murphy, J. Electroanal. Chem. Interfacial Electrochem., 109, 199 (1980).
30. L. D. Burke, M. E. Lyons, E. J. M. O’Sullivan, and D. P. Whelan, J. Electroanal. Chem. Interfacial Electrochem., 122, 403 (1981).
31. L. D. Burke and J. F. Healy, J. Electroanal. Chem. Interfacial Electrochem., 124, 327 (1981).
32. M. Ammann and J. Fransaer, Chem. Commun., 48, 2016 (2012).