RESEARCH ARTICLE



Thin-film electrochemical sensor electrode for rapid evaluation of electrolytic conductivity, cyclic voltammetry, and temperature measurements

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Received: 14 January 2015/Accepted: 25 May 2015 © Springer Science+Business Media Dordrecht 2015

Abstract A thin-film electrochemical sensor electrode capable of electrolytic conductivity, cyclic voltammetry, and temperature measurements of electrolyte solutions has been fabricated and characterized. The electrode fabrication and calibration is detailed, showing accuracies of ± 6 % for electrolytic conductivity measurements over the range of $0.1-100 \text{ mS} \cdot \text{cm}^{-1}$ and temperature measurement within \pm 2 °C from -60 to 95 °C. The electrode's capabilities are verified with standard Li-ion battery and electrochemical double-layer capacitor electrolytes, to which the measured data match well with literature values. Lastly, demonstration of the electrode's capabilities is shown with determination of cyclic voltammetry curves and electrolytic conductivity over a range of temperatures for other electrolyte solutions. Integration of these three measurement tools into a single, low-cost, high accuracy, rapid measurement electrode can greatly simplify quantitative characterization of novel electrolytes developed in the electrochemical energy storage field.

Keywords Electrochemical thin-film sensor · 4-Probe electrolytic conductivity measurement · Thin-film resistance temperature detector · Battery electrolyte · Electrochemical capacitor electrolyte

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1 Introduction

There is currently a large effort to increase the energy density of batteries and electrochemical double-layer capacitors (EDLCs) for applications ranging from electronics to powering vehicles. While developing higher voltage and highcapacity electrodes is necessary to increase the energy density of batteries, it is generally accepted that the electrolyte limits the adoption of these new electrodes [1-4]. Similarly, the electrolyte breakdown can limit the maximum voltage and energy density of an electrochemical doublelayer capacitor [5-7]. In addition to developing a wider potential electrolyte, the electrolytic conductivity must also be high enough for the device to deliver suitable power. Lastly, the potential window and conductivity of electrolytes over a broad range of temperatures are important parameters in determining the end performance of a device. These measurements are frequently performed separately with different equipments [3, 7–9], however, having a single measurement electrode to measure both the potential window and conductivity without the need for different measurement apparatus would be a useful tool to quickly collect data on a number of electrolyte solutions.

Despite being routine methods, there is often some difficulty in electrolytic conductivity and cyclic voltammetry measurements of electrolyte solutions. Electrolytic conductivity measurements are highly sensitive to the temperature, cell constant, electrode fouling, measurement frequency, and circuitry [10, 11], and can be costly or difficult to maintain. Further, commercial equipment may give inaccurate readings over a large range of conductivities [12]. Cyclic voltammetry measurements are often made difficult by a need for careful placement of electrodes in solution and the high cost of noble metal electrodes. Making accurate temperature measurements of the

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electrolyte solution during data collection also requires the solution to come to thermal equilibrium with the thermal measurement point, which could take several minutes. Attempting to place the temperature probe inside the solution near the measurement electrode could also lead to unavoidable interference with diffusion currents across the solution under study, lowering the accuracy of measurements. Finally, an expensive or difficult to synthesize electrolyte commonly limits researchers in the number of experiments that they may run due to the limited volume of solution available to work with [9, 13].

While thin-film conductivity sensors could simplify these measurements, they have been investigated primarily for sea water sensing [14–16]. Combination of electrolytic conductivity measurements with cyclic voltammetry capability has been investigated for lab-on-a-chip devices for applications in environmental monitoring in sea water [11], but an integrated temperature sensor with these capabilities has not been studied previously. Further, detailed fabrication and calibration analysis of these electrodes, and application with electrolytes for electrochemical energy storage, have not been shown. Presented here is the fabrication, calibration characterization, and demonstration of a new multifunctional, low-cost thin-film electrochemical sensor electrode capable of electrolytic conductivity and cyclic voltammetry measurements with simultaneous temperature measurement via an on-chip resistance temperature detector (RTD) sense device, tools which have not previously been integrated into a single electrode.

2 Materials and methods

2.1 Electrode fabrication

While there are a range of thin-film materials to fabricate a thin-film electrode, such nickel or copper, many of these may oxidize easily and can be difficult to maintain a clean surface. Gold is an excellent electrode material, but typically shows a lower limit than platinum to the applied oxidation potential. Platinum was chosen as the active film in the fabricated electrodes since this material (1) shows good chemical inertness over a wide potential range, (2) is easy to clean and with no oxide surface formation, and (3) has a very linear temperature coefficient of resistance, ideal for the integrated RTD device.

Electrode wafers were made by typical semiconductor fabrication techniques. Borosilicate glass slides $(75 \times 50 \times 1 \text{ mm}, \text{ average surface roughness } R_a = 9 \text{ nm},$ Fisher Scientific) were used as wafer substrate and were cleaned by successive sonication in acetone, isopropanol, and ethanol, dried under a stream of nitrogen gas and heated to 125 °C on a hot plate for 5 min to dehydrate the

surface, followed by an O₂ plasma clean for 5 min at 200 W power and 200 mT pressure (Technics PEIIB Planar Etcher). Photoresist (Futurrex NR9 1500PY) was then applied to the wafer via spin coating and the electrode pattern was then transferred via photolithography (Karl Suss MA6 Mask Aligner) followed by thin-film sputter deposition (Denton Discovery 18) onto the patterned wafer. A 10-nm-thick titanium adhesion layer was first sputter deposited followed by a platinum metal layer of various thicknesses, followed by lift-off by sonication in acetone. Cleaning of the wafer by sonication in solvent, drying, O₂ plasma clean, and application of photoresist was then repeated, as described above. A second pattern, exposing only the RTD and base of the electrochemical electrodes for passivation, was then transferred to the photoresist. Passivation of portions of the platinum film was done by sputter deposition of a second 10-nm-thick titanium adhesion layer followed by a 250-nm-thick silicon dioxide passivation layer. All thin-film sputter depositions were done in an argon atmosphere with a base pressure of 5 μ T and a sputter pressure of 2.5 mT for titanium and platinum and 4.5 mT for silicon dioxide. Electrode patterning and dimensions are shown in Fig. 1a, and with more detail of the platinum electrodes configurations used in electrolytic conductivity measurements shown in Fig. 1b. Thin-film thickness measurements (Veeco Dektak 150) were an average of five data points over a wide area with uncertainties given as the maximum deviation from the average measurement.



Fig. 1 a Patterning and dimensions for thin-film electrochemical sensor electrode and \mathbf{b} dimensional detail of the electrodes used for electrolytic electrochemical conductivity measurements

After fabrication, the wafer was diced into individual electrodes; typically one wafer yielded four electrodes. The diced electrodes were then annealed in a tube furnace under an argon atmosphere at 350 °C for 2 h with a ramp rate of 5 °C min⁻¹. Electrical connections were made to the fabricated electrode by soldering Kapton insulated wires to platinum solder pads. The solder joints were then sealed with two separate epoxies. First, a flexible epoxy (Armstrong A-12) was applied and cured on the glass substrate, followed by application and curing of a harder epoxy (Loctite 20NS). Epoxy curing was typically done at ca. 80 °C. The use of the dual-epoxy system prevents cracking of the glass substrate at extreme temperatures due to the thermal expansion mismatch between the epoxy and glass. Care was taken during epoxy application to make sure the solder joints and solder pads were completely insulated with epoxy and that the active platinum electrode areas were not covered by any epoxy. Kapton insulated wires and Loctite 20NS epoxy were both used for their good chemical resistance to solvents and thermal stability.

2.2 Measurement apparatus

Block diagrams of electrical connections between the fabricated electrode and the measurement equipment, along with the corresponding solder pad number designations, are shown in Fig. 2. While the RTD device had its own separate electrical connections, electrolytic conductivity and cyclic voltammetry measurements shared electrical connections and were switched between equipment for measurement. For RTD measurements, two wires were soldered to each electrode pad #1 and #7 for four-wire resistance measurements, made by an Agilent 34970A Data Acquisition Unit with a 34902A Multiplexer Module, shown in Fig. 2a. The RTD was calibrated by placing a Type-K thermocouple (Omega Engineering) in intimate



Fig. 2 Block diagrams showing electrical connections between the electrode pads and measurement equipment for \mathbf{a} RTD, \mathbf{b} cyclic voltammetry, and \mathbf{c} electrolytic conductivity measurements

contact with the electrode and making simultaneous temperature and RTD resistance measurements across a range of temperatures. The thermocouple measurement was accurate to ± 2 °C and was most significant source of error in RTD measurements.

Cyclic voltammetry measurements were made by connection of the counter, working, and reference electrodes, and electrode pads #2, 4, 5, respectively, to a Bio-Logic SP200 potentiostat, shown in Fig. 2b. The counter, working, and reference electrodes had geometric areas of 21.62, 1.00, and 1.95 mm², respectively. On occasion, a separate lithium metal reference electrode was introduced into solution, connected to a separate wire, while the platinum reference electrode was unused for cyclic voltammetry measurements. Since the small size of the electrodes could introduce a significant voltage drop [17], iR-drop software compensation was used for all cyclic voltammetry measurements.

Electrolytic conductivity measurements were made using a custom built impedance analyzer, schematically shown in Fig. 2c. A floating AC current signal from an Agilent 33120A 15 MHz Function Generator was passed through the electrolyte solution via the current electrodes, pads #2 and #6. Two separate electrodes, pads #3 and #5. were used to sense the voltage between the current electrodes, typically 10-20 mV_{rms}. Current measurements were made by measurement of the voltage drop across a 50 Ω thin-film resistor which the AC current was passed through. A thin-film current sense resistor was used since it has little capacitive or inductive behavior at the frequencies measured. The geometric areas of the current and voltage electrodes were 21.62 and 1.95 mm², respectively. To reject common noise, amplify the voltage signals and avoid ground loops through the electrolyte, the voltage across both the current sense resistor and across the sense electrodes were measured differentially through two separate Tektronix ADA400A Differential Preamplifiers, which then sent the voltage measurements to a Tektronix TDS1000 Oscilloscope. It was verified that the preamplifiers did not significantly attenuate the signals across the frequencies used. Cell constant calibrations were done from 1 MHz to 100 Hz, while electrolytic conductivity measurements were typically done at a frequency of 1 kHz, which generally showed a phase angle between -5 and 0° for all measurements.

Electrolytes were all prepared under argon atmosphere and bubbled with argon gas to remove trace oxygen for at least 5 min immediately prior to using. The measurement electrode was fixed to a screw-on cap of a 20 mL glass vial, in which the electrolyte solution was contained and all measurements were performed. Careful placement of the electrode in the center of the vial was done in order to avoid changing fringe field effects from modifying the calibrated cell constant for electrolytic conductivity measurements. Electrolyte solution volume was kept constant for all experiments and covered the entire measurement electrode's surface. After electrolyte and electrode preparation, the assembly was transferred to a temperature chamber where measurements were performed.

Data acquisition and hardware control were done via LabView software. Typically, temperature and electrolytic conductivity measurements were made at a rate of one data point every few seconds. This allowed for rapid measurements of electrolytic conductivity over a wide range of temperatures.

2.3 Chemicals

For electrolytic conductivity measurements, the electrode cell constant was calibrated with potassium chloride conductivity standards (NIST-traceable) from Cole Parmer. Tetraethylammonium tetrafluoroborate (TEABF₄, electrochemical grade, >99 %), tetrabutylammonium hexafluorophosphate (TBAPF₆, electrochemical grade, >99 %), lithium hexafluorophosphate (LiPF₆, battery grade, >99.99 %), ethylene carbonate (anhydrous, >99 %), dimethylcarbonate (anhydrous, >99.9 %), tetrahydrofuran (anhydrous, >99.9 %), dichloromethane (anhydrous, >99.8 %), propylene carbonate (anhydrous, >99.7 %), and acetonitrile (anhydrous, >99.9 %) were all purchased from Sigma-Aldrich.

3 Results and discussion

3.1 Resistance temperature detector calibration

To verify consistent sputter deposition rates of the thin films, platinum and titanium adhesion layer thickness measurements were made with various platinum deposition times, shown in Fig. 3. An excellent linear relation is found ($R^2 > .999$) for platinum deposition times from 50 to 300 s with a deposition rate of 0.87 \pm 0.02 $\rm nm\cdot s^{-1}.$ The titanium adhesion layer deposition was held constant through all depositions and is found to be 10.74 ± 4.18 nm thick. The low surface roughness of the glass substrate was not expected to create discontinuities in the platinum RTD element. However, since any inadvertent discontinuities in the thin film that might arise from insufficient film thickness would lower measurement accuracy and give less linearity between resistance and temperature readings, the effect of RTD element film thickness on electrical resistance was studied. Calibration curves of multiple RTD elements of different platinum thin-film



Fig. 3 Thin-film thickness as a function of platinum sputter deposition time with a titanium adhesion layer, as described in Sect. 2.1 of the text



Fig. 4 Resistance as a function of temperature for four RTDs of various platinum thin-film thicknesses

thicknesses are shown in Fig. 4 for a temperature range of -60 to +95 °C. The calibration curves for all film thicknesses show excellent linearity ($R^2 > .999$ for all curves) over the entire temperature range measured, as is commonly exhibited by platinum RTDs [18]. A good indication of uniformity and purity of the platinum RTD may be shown by the value of the thermal coefficient of resistance (TCR), calculated by

$$TCR = \frac{1}{R_{ref}} \cdot \frac{dR}{dT},$$
(1)

where R_{ref} in Eq. 1 is the resistance at a reference temperature of 25 °C. Despite the good linearity of the platinum RTD elements, the calculated values of the TCR, shown in Table 1 for various platinum film thicknesses, differ by roughly a factor of two from the accepted value of 3926 ppm K⁻¹. This difference may be due to the relatively thin-film thickness, diffusion of the titanium adhesion layer through the platinum, and grain boundaries that may exist in the thin-film RTD.

Thickness/nm	Resistance at 25 $^{\circ}C/\Omega$	d <i>R</i> /dT	TCR/ppm K ⁻
54	4870	7.00	1437
91	2313	4.10	1772
136	1450	2.84	1961
268	1030	2.12	2060

Table 1 Platinum RTD properties calculated from data in Fig. 4

The resistance stability of two different RTDs of thicknesses of 136 and 268 nm at 85 °C in air is shown in Fig. 5. The RTDs show less than 0.015 % change in resistance over 80 h at this elevated temperature, showing the excellent temperature stability of the devices. Further, the largest fluctuations in the devices are correlated to the night-day temperature change in the laboratory from which the measurement electronics have a slight measurement change, showing that the actual stability of the RTDs is likely much better. Routine cleaning by sonication in solvents, gentle wiping, and soaking in various solvents at elevated temperatures similarly showed little or no change in the RTD calibration. Thus, the highly stable properties of the platinum RTD allow it to be reused routinely without need for repeated calibration.

3.2 Electrolytic conductivity calibration

In contrast to metals, in which electrons are the primary charge carriers, electrolytes conduct current through transport of ions, therefore typical DC electrical resistance measurements are not possible. In order to minimize capacitive effects via charge build up at the electrode surface, an AC method must be utilized for electrolytic conductivity measurements. For the thin-film electrochemical



Fig. 5 Resistance stability of two platinum RTD elements over time while held at 85 °C in air

sensor electrode, a four-electrode measurement method, rather than a two-electrode measurement method, was chosen for conductivity measurements in order to avoid electrode contamination with reduced or oxidized species at the electrode surface and have higher measurement accuracy across a wide range of solution conductivities. To make electrolytic conductivity measurements, an alternating current is passed through the electrolyte between two outer electrodes and the voltage drop is sensed between two inner electrodes. The voltage sense electrodes were configured to be significantly narrower than the current electrodes such that the electrolytic current induced was as uniform as possible across the voltage sense electrodes.

Two electrodes passing a current through an electrolyte solution may simply be modeled as two RC circuits in series. The first RC circuit comprises of the electrolyte resistance and bulk electrolyte capacitance, R_b and C_b , followed by the second RC circuit comprised of the charge-transfer resistance and double-layer capacitance, R_{ct} and C_{dl} , between the electrode and electrolyte interface. Depending on the particular values of these resistive and capacitive components, one or two semi-circles may be formed in the corresponding Nyquist plot. The measured bulk electrolyte resistance would correspond to the real component of the impedance where the phase goes to zero toward the end of the first semi-circle.

To calibrate the cell constant of the measurement electrode, four different potassium chloride electrolyte conductivity standards of 0.1, 1, 10, and 100 mS·cm⁻¹ were used and impedance and phase measurements were recorded across a range of frequencies from 1 MHz to 100 Hz. Figure 6a shows the phase angle of the impedance vector versus frequency and it is seen that higher conductivity solutions go to zero phase angle at progressively higher frequencies. Similarly, higher conductivity solutions show less change in the real component of the impedance, Z', over a wider frequency range, as shown in Fig. 6b. These features are common in electrolyte solutions, as explained elsewhere [10]. A Nyquist plot for each calibration solution is shown in Fig. 6c with the points near zero phase angle, where resistance measurements are taken, marked with the corresponding frequency. Some features shown in the Nyquist plots, such as negative real impedance and inductive behavior, are commonly seen in such measurements and are generally disregarded as artifacts from the measurement hardware [10].

The cell constant, needed to determine the conductivity of an electrolyte, is very dependent on the geometrical configuration and surface area of the measurement electrodes, as well as the geometry and material (electrically insulating or conducting) of the electrolyte container, and calibration is generally done routinely before measurements. By

Fig. 6 a Phase and b real impedance measurements versus frequency and c Nyquist plots of standard KCl electrolytic conductivity calibration solutions at 25 °C



correlating the measured electrolytic resistance, units of Ω , of each solution to the solutions NIST-traceable calibrated conductivity (κ), units of S·cm⁻¹, one may determine the measurement electrode's cell constant, *K*, units of cm⁻¹. Typically, the simple relation is given as

$$k = K \cdot R^Q, \tag{2}$$

where R is the measured electrolyte resistance and, typically, Q = -1. Equation 2 is used to fit the electrolytic resistance data points in Fig. 7 for each calibration solution with the fit parameters detailed in Table 2. When the constant Q is set to -1, as routinely done through the literature [19, 20], the error of the fit is found to be approximately 0.14 and 60 % at solution conductivities of 100 and 0.1 mS·cm⁻¹, respectively. While this broad range of conductivity is not typically easy to measure accurately even with commercially available equipment [12], measurement accuracy across the full range of conductivities should be improved. By allowing the constants Q and K to be simultaneously fit to the measured data, a significantly improved accuracy is obtained. Fitting constant Q to only a slightly different value, Q = -1.071, improves the accuracy to within \pm 6 % error over all conductivity solutions



Fig. 7 Measured electrolyte resistance versus actual conductivity of the standard KCl electrolytic conductivity calibration solutions at $25 \, ^{\circ}$ C with the corresponding measurement frequency

used, accounting for four orders of magnitude, as detailed in Table 3. It is possible this new fitting parameter for finding the cell constant could greatly improve accuracy of other conductivity measurement equipment over a wider range of electrolyte conductivities. Although not studied in detail, it is believed that the fitting parameter Q is highly

Table 2 Cell constant values fit to the equation $k = K R^Q$

Parameters	Q = -1	Q = fit
K	0.407 ± 0.003	0.463 ± 0.001
Q	-1.000	-1.071 ± 0.002

 Table 3 Percent error of calculated conductivity with actual conductivity

Conductivity/mS·cm ⁻¹	Q = -1	Q = fit	
0.1	-60.19	-4.51	
1	-25.09	5.60	
10	-12.01	1.28	
100	0.14	-2.75	

dependent on fringe field effects created by the container size and shape holding the electrolyte solution.

3.3 Verification of measurement electrode calibration

To verify the measurement electrode's electrolytic measurement accuracy over a wide range of conductivities and temperatures, measurements of a standard lithium battery electrolyte (1.0 M LiPF₆ in ethylene carbonate and dimethylcarbonate, 1:1 by wt) and a standard electrochemical double-layer capacitor electrolyte (1.0 M TEABF₄ in acetonitrile) were made and compared to literature values [3, 21, 22], shown in Fig. 8a. The accuracy of the measurements, over a wide conductivity from 3 to 76 mS·cm⁻¹ and from -35 to 75 °C, are in close agreement with the literature values. The percent difference in the conductivity measurement as compared with literature values is shown in Fig. 8b. The measurement error for the

Fig. 8 a Comparison of and b percent difference between measured and literature values of two common electrolyte solutions over a wide temperature range. Literature data replotted in (a) with permission from references [3, 21, 22]

lithium based electrolyte is less than 4 %, within the \pm 6 % error determined earlier for the calibrated thin-film electrode. However, the error for the acetonitrile based electrolyte is in 6–7 % error with literature values. This discrepancy is probably due to the measurement error in the comparative data, which is not given in their work [21, 22].

Cyclic voltammetry curves of the lithium based electrolyte were also performed in order to verify electrode behavior at higher current densities at a range of temperatures, as shown in Fig. 9 (only anodic currents shown for clarity). The sharp change in current near 0 V versus Li is due to the lithium plating onto the platinum electrode, and the small peak at 0.7 V versus Li is due to lithium stripping off of the platinum electrode. Other features at 2.0 and 3.5 V versus Li are thought to be due to impurities (O_2, O_3) H_2O , etc.) in the electrolyte [22, 23]. Cyclic voltammetry curves were also taken at various temperatures, also shown in Fig. 9. There is a clear increase in current at higher temperatures due to the increased diffusion within the electrolyte and a lower energy barrier for chemical reactions to occur. Cyclic voltammetry studies at various temperatures is an excellent method to observe electrochemical kinetics with detail, though it is not a common technique used in the literature.

3.4 Characterization of electrolytes with thin-film electrochemical sensor electrode

A group of four electrolytes were used to demonstrate the ability to determine the potential window and electrolytic conductivity with the thin-film measurement electrode. The four electrolytes all consisted of 0.1 M tetrabutylammonium hexafluorophosphate in various solvents: tetrahydrofuran, dichloromethane, propylene carbonate, and acetonitrile. Cyclic voltammograms for the four electrolytes at room temperature are shown in Fig. 10a, along





Fig. 9 Cyclic voltammetry curves of 1 M LiPF₆ in EC:DMC (1:1 by wt.) over a range of temperatures with a 100 mV·sec⁻¹ sweep rate, platinum working, and counter electrodes, and a lithium metal reference electrode. Only anodic currents shown for clarity

with their reduction potential, oxidation potential, and total potential windows listed in the inset. A cutoff current of $1 \text{ mA} \cdot \text{cm}^{-2}$ was used to determine the limiting potentials. It is important to note that this current, while commonly used in the literature, is an arbitrary value and is also dependent on the potential sweep rate used.

The conductivity of the same four electrolytes was also examined at a broad temperature range, shown in Fig. 10b. As expected, the acetonitrile based electrolyte has a significantly higher conductivity than the others due to the solvent's low viscosity, which increases ion mobility within the electrolyte. While having an overall lower conductivity than acetonitrile, dichloromethane and tetrahydrofuran have a much lower freezing points (-97 and -108 °C, respectively) versus acetonitrile (-45 °C) and show good conductivity as low as -60 °C. Propylene carbonate, while having excellent electrochemical stability, often shows low electrolytic conductivities due to the high viscosity of the solvent.

4 Conclusion

A thin-film electrochemical sensor capable of temperature, ionic conductivity, and cyclic voltammetry measurements has been fabricated and characterized, and offers a lowcost, simple device capable of making critical high accuracy electrochemical measurements rapidly over a wide temperature range and wide electrolytic conductivity range. The design and fabrication techniques have been detailed and the device would be simple to fabricate for any researcher with standard thin-film fabrication equipment. Contrary to the conventional method of waiting a number of minutes for thermal equilibrium to make measurements, an on device RTD has been fabricated and capable of determining the temperature right at the point of measurement, which enables rapid measurements rather than waiting for thermal equilibrium between the electrolyte and thermal measurement device outside the solution. Electrolytic conductivity measurement calibration has also been described with a new method of calculating the electrode cell constant with accuracy of \pm 6 % for electrolytic conductivity over a range of 0.1 to 100 mS \cdot cm⁻¹ which, to the authors knowledge, is the highest accuracy shown over such a wide range. The temperature and electrolytic conductivity calibrations have been verified by measuring two standard electrolytes and comparing with literature values. Cyclic voltammetry curves over various temperatures for an electrolyte have also been shown and can be a useful technique to observe in more detail certain electrochemical kinetics. Lastly, demonstration of the electrode measurements with four other electrolytes with cyclic voltammetry and electrolytic conductivity over a range of temperatures has been shown. With a number of new solvents and salts with applications in the rapidly growing field of electrochemical energy storage, accurate and rapid electrochemical characterization is often necessary and the described thin-film electrochemical sensor





electrode could greatly simplify these processes with improved measurement accuracy.

Acknowledgments The authors acknowledge financial support of this work by DOE ARPA-E Grant No. DE-AR0000379 and by Iwama Fund at UC San Diego and helpful discussions and fabrication assistance with the Nano3 Cleanroom staff Sean Parks and Ivan Harris at UC San Diego.

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