Thermochimica Acta 653 (2017) 8–15

Contents lists available at ScienceDirect

Thermochimica Acta

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

A novel apparatus for coulometric titrations in lithium containing systems

A. Beutl*, S. Fürtauer, H. Flandorfer

Institute of Inorganic Chemistry–Functional Materials, University of Vienna, Althanstraße 14 (UZA 2), A-1090 Wien, Vienna, Austria

ARTICLE INFO

Keywords:
Coulometric titration
EMF measurements
Instrumental setup
Apparatus
Li systems
Li-Sn

ABSTRACT

The thermodynamic description of Li containing systems is readily accessible by coulometric titrations in combination with EMF measurements. Although this method is often encountered in literature, the experimental apparatus needed is in general only poorly described. As Li and its alloys are very reactive substances, many parameters like the materials used for the electrochemical cell, cell geometry, establishment of O_2- and H_2O-free atmosphere, etc. are all important factors for a successful measuring device. Therefore, an instrumental setup for coulometric titrations combined with EMF measurements is presented in detail, covering the general and the electronic setup used, as well as the structure of the electrochemical cell. The apparatus is validated with two measurements conducted in the Li-Sn system, which are further compared with literature data.

1. Introduction

For the thermodynamic description of Li-containing intermetallic systems, a purely metallurgic approach is often not possible, or at least not feasible due to the limited choice of proper materials for containment of the components and alloys. Their high reactivity restricts the materials suitable for sample preparation to expensive and difficult to machine ones, e.g. Mo, Ta, W or MgO. Additionally, sample containers prepared by these materials can only be used for one distinct sample and then have to be discarded. Therefore, a generally more accessible way to investigate Li-containing systems is by means of electrochemistry. The so-called coulometric titration can be used to change the Li content of a sample meticulously, depending on the amount of charge applied, according to the following reactions:

$$y\mathrm{Li} \rightarrow y\mathrm{Li}^{+} + ye^{-} \quad (1)$$

$$X + y\mathrm{Li}^{+} + ye^{-} \rightarrow \mathrm{Li}_{y}X \quad (2)$$

For these reactions, a Li source and a sample material (X) have to be connected by a Li-ion conducting electrolyte. Furthermore, a potentio-/galvanostat has to be used to enable the precise control of the applied charge. The time (t) and amount of current (I) flowing between the sample (working electrode: WE) and the Li source (counter electrode: CE) is measured and the amount of charge (Q) applied to the system can be then calculated as follows: $Q = \int_0^t I(t)dt$.

To determine the molar amount of Li (n_{Li}) deposited onto the WE, respectively removed from the WE, Faraday's law can be applied: $n_{Li} = \frac{Q}{F}$ where F is Faraday's constant. Thermodynamic data of the occurring electrochemical reactions can be obtained by measuring the equilibrium potential, ΔE, *i.e.* the electro motive force (e.m.f.) between the WE and an additional reference electrode (RE). This so-called three-electrode set up avoids obtaining tampered potentials by polarization of the CE. Performing these kind of measurements at different temperatures, allows the determination of partial thermodynamic quantities apart from the Gibbs energy like entropy and enthalpy [*cf.* 1]. However, by measuring ΔE with respect to compositional changes, enabled by the coulometric titration technique, it is also possible to obtain integral thermodynamic quantities directly from the measurements. This was already pointed out in detail by [2]. Thus it is possible to directly measure *e.g.* Gibbs energies of formation for intermetallic compounds, etc. Coulometric titrations in this sense were first introduced in 1953 by Wagner [3] for the Ag-S system. Due to its feasibility, it was readily adopted for Li containing alloys. Thus investigations in different intermetallic systems were conducted, e.g. Li-Al [4], Li-Sb [2], Li-Sn [5], Li-Cu [6] and others.

However, there are also many challenges posed by this method, which have to be attended.

- During coulometric titrations, Li is only deposited onto the surface of the sample. Therefore, diffusion of Li into the sample is necessary to form a homogenous alloy, which is the prerequisite to measure the equilibrium potential ΔE at the respective Li concentrations. Thus, the diffusion rate of Li has to be high to provide fast kinetics. In order to increase the rate of diffusion, the temperatures of the measurements can be increased; generally they lie between 400 °C

---

* Corresponding author.
E-mail address: alexander.beutl@univie.ac.at (A. Beutl).

http://dx.doi.org/10.1016/j.tca.2017.03.025
Received 21 February 2017; Received in revised form 28 March 2017; Accepted 29 March 2017
Available online 31 March 2017
0040-6031/ © 2017 Elsevier B.V. All rights reserved.

and 600 °C.

- Li and Li containing alloys are highly reactive materials that often can only be handled in an air and moisture free environment. Therefore, the cell has to be sealed gas tight when the measurements cannot be conducted in a glovebox. The materials for the cell have to be chosen carefully, as ceramic materials such as alumina and boron nitride (BN) are not stable when in contact with Li. Amorphous materials too, such as silica glass, show reactions with Li. The reactivity is additionally increased due to the elevated temperatures applied for the measurements.
- Another difficulty is to measure several parameters, like potential difference between the WE and RE, current between WE and CE, or temperature, in a closed cell.

Thus, the main issue concerning coulometric titrations in Li containing systems is the instrumental setup and it’s assembling. Therefore, an elaborated cell design and a careful selection of materials is a prerequisite for proper measurements. However, in literature [2,4–6] this point is often only poorly described and crucial aspects about the measuring setup are not reported. Based on this scarce information it is not possible to construct such an experimental setup without months of elaborate and costly trial and error developments. Therefore, this work is dedicated to present an experimental setup for coulometric titrations in detail, discussing the experimental apparatus, as well as difficulties and compromises made between the chemical stability of the cell and technical feasibility.

2. The apparatus

2.1. General setup

The general setup of the measurements is depicted in Fig. 1. The measuring cell is immersed into a tube furnace, which is controlled with a PID-controller Eurotherm 3508. The controller is connected to the central computing station (PC) via Ethernet connection. The different electrodes, WE, CE and RE are connected to two digital multimeters (DMM) and two power supplies. The electric wiring is discussed in more detail in the next section. All measuring devices as well as power supplies are connected to the PC from which the different parameters of the measurement can be controlled via LabView (National Instruments) based on graphical programming. A vacuum pump and Ar supply are directly attached to the measuring cell to enable measurements in Ar atmosphere. Evacuation and flushing with Ar has to be done manually.

2.2. Electronic setup

The electronic measurement setup is shown in Fig. 2a and is similar to the one used by Wagner [3]. The heart of the measurement is composed of a Keithley 2000 DMM, with 6 1/2 digits, a National Instruments (NI) PXI-1033 chassis, containing three different modules, a NI PXI-4071 DMM with 7 1/2 digits, a NI PXI-2501 multiplexer including 4 × 6 matrix terminal block TB-2606 as well as a NI PXI-4110 DC power supply card. Additionally a NI USB 6008 data acquisition device (DAQ) with two analogue outputs is used. The chassis is connected to the PC via a PCI-Express respectively MXI-Express connection.

The NI PXI-4110 power supply card is composed out of three separate channels A, B, C, ranging from A: +6 V to 0 V, B: +20 V to 0 V and C: −20 V to 0 V. All channels are able to deliver currents up to 1 A. The positive terminal of channel C and the negative terminal of A are directly connected to the WE and are used to either apply a positive or a negative potential pulse. The respective other terminal is connected with the counter electrode via reed relays R1 or R2, which necessarily have a very low resistance (~1 Ω) compared to the electrolyte (several hundreds Ω) in order to avoid the formation of a voltage divider. To deposit Li at the WE, R1 is closed and R2 remains open, whereas Li is removed from the WE, if R2 is closed and R1 remains open. If no potential is applied, both R1 and R2 are open. Thus, the potential can be measured without disturbances. The two relays are operated by the remaining power supply (B) on the NI PXI-4110 card and the analogue output of the NI USB-6008 DAQ. The NI USB-6008 DAQ device is connected to the PC via USB interface. The Keithley 2000 DMM is connected in serial with the counter electrode to measure the current flowing through the cell. It is connected via RS232 interface with the PC. The NI PXI-4071 DMM is used to measure the voltage between the WE and CE, the WE and RE and between the two contacts of the thermocouple TC+ and TC-. Furthermore it measures the resistance of the thermistor TΩ. The multiplexer card NI PXI-2501 (inner resistance approx. 3–4 kΩ) is used to switch between the different contacts, as shown in Fig. 2b, and is because of the comparable high inner resistance

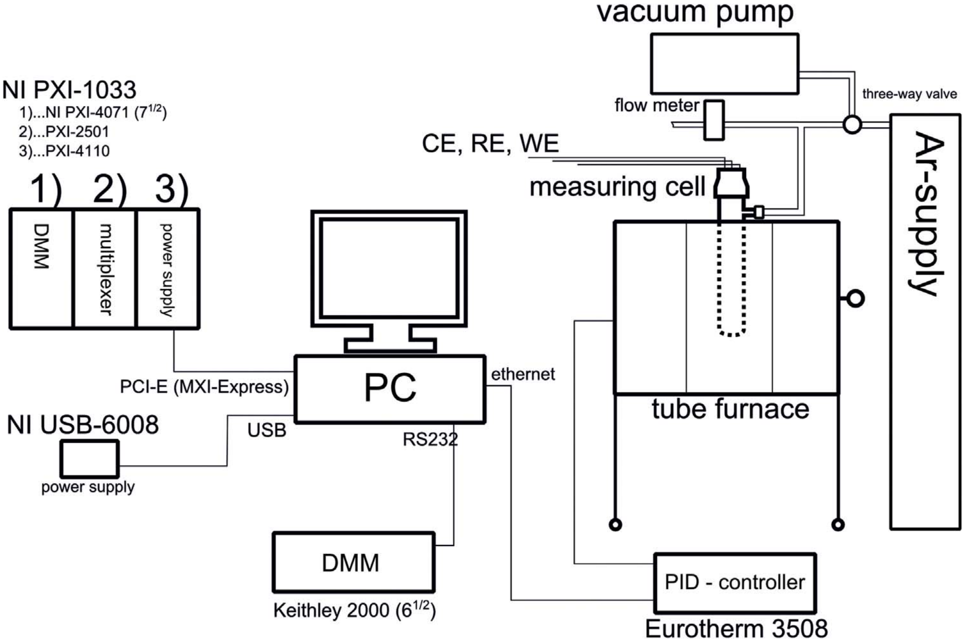

Fig. 1. General setup of the coulometric titration measurements.

Download English Version:

https://daneshyari.com/en/article/4995893

Download Persian Version:

https://daneshyari.com/article/4995893

Daneshyari.com